Polycyclic and Oligocyclic Phosphorus-Nitrogen Ring Systems

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Publikationen

1. Symmetrical Bis-Phosphorus Compounds and Macrocycles with two 1,3,2-Benzodiazaphosphorinone Units - Oxidation and X-Ray Structure Analysis of Selected Compounds
Z. Anorg. Allg. Chem. **2000**, *626*, 969-974.

2. New Bifunctional Benzoxazaphosphorinane Systems
Z. Anorg. Allg. Chem. **2002**, *628*, 274-278.

3. New Phosphorus-Containing Polycylic Large-Ring Systems Involving Heteroatoms
Z. Naturforsch. **2002**, *57b*, 1008-1016.

4. Synthesis of Ethylene-bridged Heterocyclic Bidentate P(III)N - Ligands - Oxidation and Complexation Studies
Z. Anorg. Allg. Chem. **2003**, *629*, 1953-1959.

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1. Introduction

1.1. Phosphorus

The element phosphorus was discovered in 1669 by the alchemist Hennig Brand of Hamburg by distillation of urine [1]. In fact, no less than 50-60 buckets were required per experiment, each of which took more than a fortnight to complete. The substance obtained by Brand glowed in the dark and burst into flame when exposed to air. It was subsequently named ‘Phosphorus’, meaning light-bearing.

Phosphorus is frequently misspelled as "phosphorous". It exists in several allotropic forms including white (or yellow), red, and black (or violet). White phosphorus has two modifications. Ordinary phosphorus is a waxy white solid. When pure, it is colourless and transparent. It is insoluble in water, but soluble in carbon disulphide. It catches fire spontaneously in air, burning to P_4O_{10}, often misnamed as phosphorus pentoxide. When exposed to sunlight, or when heated in its own vapour to 250°C, it is converted to the red variety. This form does not ignite spontaneously and it is a little less dangerous than white phosphorus. The red modification is fairly stable and sublimes with a vapour pressure of 1 atmosphere at 417°C [2-6].

Although phosphorus was originally extracted from urine, it is never found as the free element but is widely distributed in many minerals. Phosphate rock (apatite, impure calcium phosphate) is an important source of the element. Large deposits are found in Marocco, in Russia, and in the USA [2-6].

Phosphorus is a key component of biological molecules such as DNA and RNA. It is a component of bones, and teeth, and many compounds required for life. Each person has 1.1% of phosphorus in its body. If a person has a weight of 80 kg, then it contains 880 g phosphorus. Chronic poisoning of people working unprotected with white phosphorus leads to necrosis of the jaw ("phossy-jaw") [2-6].

Elemental phosphorus is severely toxic, the white form more so than the red form. Many phosphate esters are nerve poisons and should only be handled by a competent chemist. Inorganic phosphates are relatively harmless. Phosphate pollution occurs as a result of leached fertilisers and from many detergents [2-6].

The position of the element phosphorus lies near the center of the Periodic Table, with an electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^3$**.** Unlike its lighter analogue nitrogen in the same group in the periodic system, the phosphorus atom possesses an empty d-orbital which can engage in p_π-d_π double bonding. The special properties of tetrahedral phosphorus are believed to be the result of a degree of multiple bonding arising from the donation of non-bonding *2p* electrons from a negatively-charged substituent into the vacant 3*d* orbitals of phosphorus. The resulting p_π-d_π bonds are considerably weaker than p_π-p_π bonds because of the relatively higher energy and more diffuse nature of the 3d orbitals. The *d*-orbitals are also responsible for the existence of penta- and hexacoordinated phosphorus, e.g. in the form of PF_5 and PF_6^-, which are unknown for nitrogen. Phosphorus is known to exhibit coordination numbers from 1 to 6 and all oxidation numbers from –3 to +5 [6].

The difference of the electronic structure of N and P atoms also results in different stereochemistry [7]. In contrast to the very low inversion barriers found in acyclic amines ($E_{act} \cong 5$ kcal/mol), the energies for inversion in phosphines are much higher, of the order of 30 kcal/mol. This has permitted the preparation of numerous enantiomerically pure tertiary phosphines for which the corresponding amines are unknown [7,8].

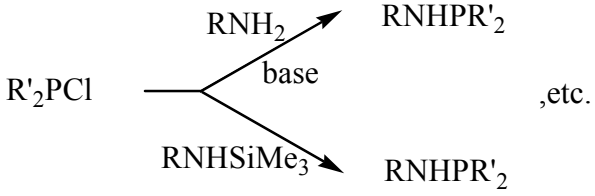
Since the discovery of the organophosphorus compound in 1897 (Me_3P from methyl chloride and calcium phosphide) numerous compounds involving phosphorus in different oxidation and coordination state have been synthesized [4]. But the significant expansion of all branches of phosphorus chemistry began only since the 1950ies, fuelled by the development of ^{31}P-NMR spectroscopy and the application of X-ray studies. Today, the study of phosphorus chemistry is becoming increasingly important. Many phosphorus compounds, especially the organic phosphorus compounds, are finding more and more applications in the pharmaceutical and cosmetics industry and agriculture. Meanwhile, many phosphine complexes are important catalysts in industrial processes.

1.2. Phosphorus-Nitrogen Chemistry

Phosphorus-nitrogen chemistry has a long history [9, 10]. Interest in compounds containing phosphorus and nitrogen, with direct bonds between the two elements, continues to increase, and they are found in increasingly diverse fields in academic research and applied

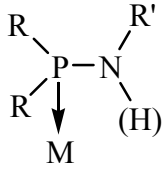
technologies [2-6] . Although traditional phosphorus chemistry is dominated by compounds containing P-O and P-C linkages (almost all naturally-occurring phosphorus compounds contain P-O bonds), P-N chemistry is undoubtedly one of the most exiting areas in main group chemistry. Apart from a steady increase in the number of new P-N compounds, greater structural insight and an improved understanding of their bonding situation, has helped to consolidate the field [11, 12].

The prototypical reaction used to form single P−N bonds involves the elimination of hydrogen chloride from the treatment of an amine with a chlorophosphine [13]. As the formation of a P−N single bond is usually facile, this standard methodology has been established and employed for many decades [13]. An alternative reaction is to employ an aminosilane which also leads to aminophosphines, but the advantage of this method is that the side-product is trimethylchlorosilane, which can easily be removed by distillation due to its low boiling point. However, the method is limited by the comparatively poor availability of aminosilane precursors [14].



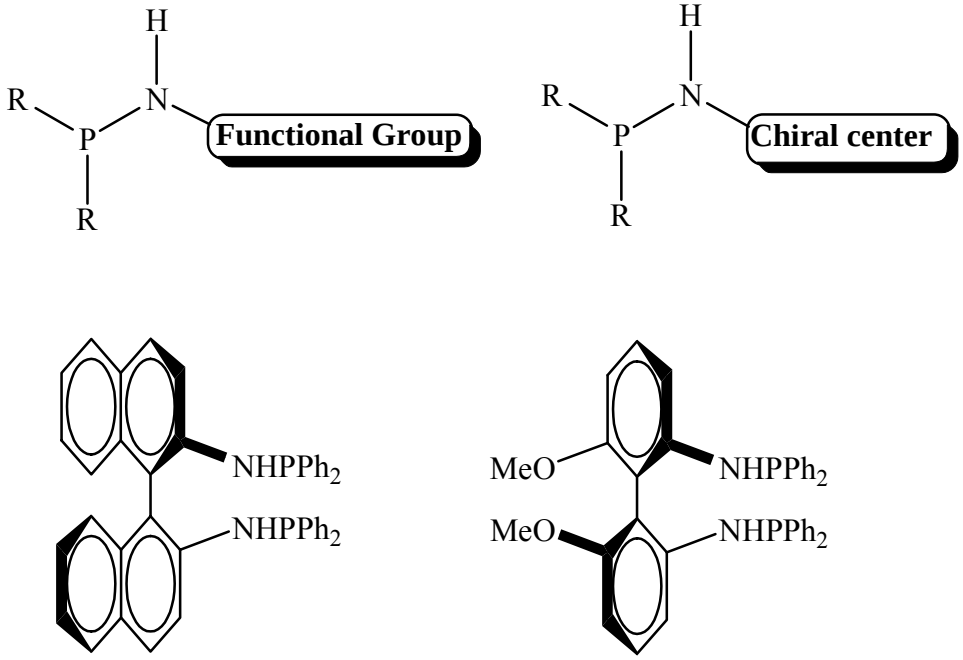
In recent years there is a trend towards utilising a route that employs inorganic bases, which employs via alkali- metallated amine intermediates, for example the lithium amide RNHLi. Compounds of type RNHM (R = alkyl or aryl; M = Li, Na or K) are important precursors in organic synthesis [15, 16]. Of the various metallated salts, lithiated amines are most common, many structures have been elucidated by X-ray crystallography. However, since many lithiated species are not very stable even at low temperature, they are often generated *in situ* and converted into the desired product. The relatively strong basic properties of such amides enable the rapid formation of the P−N bond. In particular, this methodology is especially useful for sterically bulky amines when the conventional method using organic bases like triethylamine is too slow for practical purpose [17, 18].

The established phosphorus chemistry is strongly represented by the coordination chemistry using phosphorus(III) compounds [19, 20]. Phosphorus(III) centres in any P,N compound bearing a lone pair of electrons on both the P- and N-centres, are widely used as ligands in transition coordination chemistry, and tend to coordinate via phosphorus.



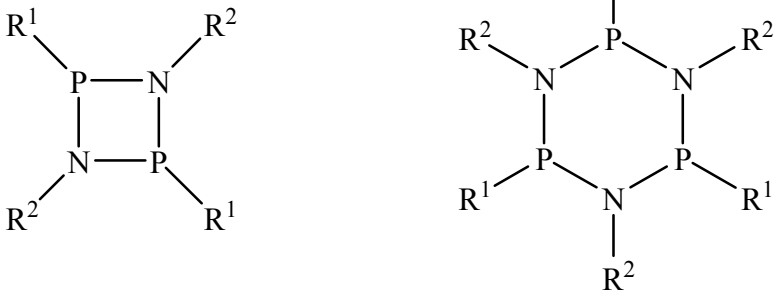
M = Transition metal

The current focus of attention in P, N chemistry is the design and synthesis of aminophosphines with functionalised groups or chiral centers. Introduction of functional groups will change the coordination mode of the P, N ligands. However, in most cases, phosphorus remains the main donor to transition metals. Due to the applications of aminophosphines as multi-functional ligands in coordination chemistry, many functionalised aminophosphines (methoxyl, pyridyl, acetyl, et. al), have been prepared recently [21]. Aminophosphines bearing chiral centers have found applications in asymmetric catalysis [22, 23]. In particular, chiral aminophosphines, BINOL-analogues combined with transition metal salts, exhibit excellent activity in asymmetric hydrogenation reactions [24, 25]. In addition, phosphinoamido complexes are excellent catalysts for the polymerization of ethylene and lactones [26, 27]. All these interests in catalytic applications have promoted further development of the aminophosphine and their related chemistry.



1.3 Phosphorus(III)-Nitrogen Heterocycles: A General View

The chemistry of numerous inorganic rings containing P(III)-N bonds, including synthesis and chemical reactivity, is well known. There are several reviews relating to this topic [28]. Despite an extensive literature, the subject of cyclophosphazanes is still at a relatively early stage of development compared with that of the cyclophosphazenes (cyclic systems, including P=N bonding). The first well authenticated simple phosph(III)azane rings were described as early as 1969, there were earlier attempts and claims, but the research on this particular subjects has suffered to an unusual degree from poor reproducibility of the results obtained by different experimenters [29, 30]. The instability of the compounds, and consequent experimental difficulties may explain the reasons. Among the numerous heterocyclic systems, four-membered ring systems with $(PN)_2$ units and derived cage compounds, due to their facile preparation, have been dominating this field in the past decades. Six-membered phosphazanes were also well studied. Few cyclophosphazanes with rings of other sizes have been reported. Reports on these systems have been explosive in the last 15 years, strongly represented by L. Stahl, X. Chievers [28]. These aminophosphines can react with numerous representatives from the main group elements and transition metal complexes. It is surprising that similar systems with larger ring size have received little attention.



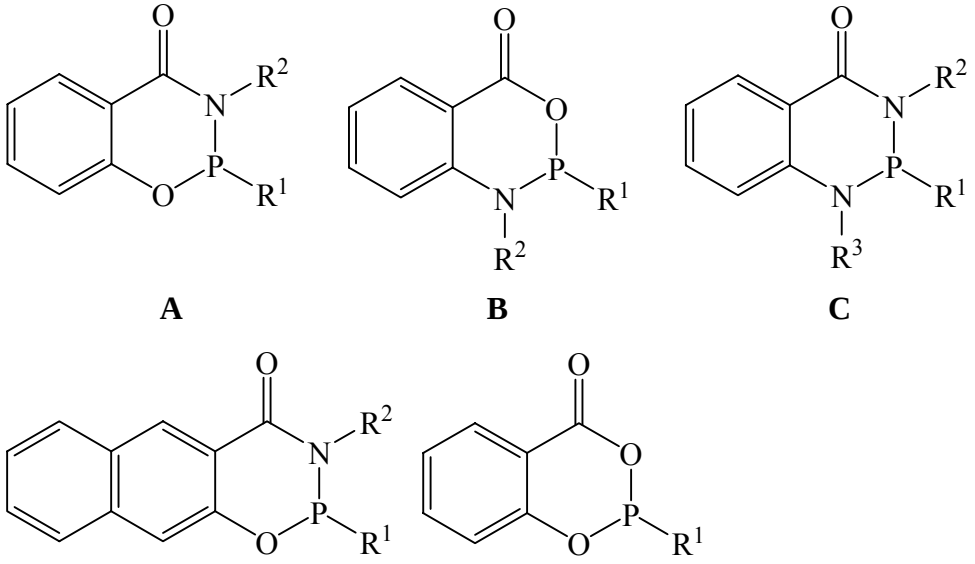
R^1, R^2 = alkyl, aryl

The properties of the phosphorus atoms in the phosphazane rings depend, generally, on the electronic structure, they show chemical properties similar to their acyclic analogues. Stereospecific properties which are specially caused by the closure of the ring systems remain the only difference between cyclic and acyclic phosphazanes. For example, small three-membered P-N ring systems are thermally less stable than their higher analogous like five-, six-membered P-N rings. Meanwhile five- and six- membered P-N rings are less air-sensitive than their acyclic analogues. Due to the pyramidal configuration of the phosphorus atom and the higher inversion energy of usual P-N there are significantly more isomeric systems known than in the case of more common inorganic ring systems with only N- or O-atoms.

1.4 Phosphorus-containing Polycyclic Ring Systems.

1.4.1. Six-memebred Cyclic Phosphazanes

Since the discovery of 5,6-benzo-2-chloro-1,3,2-diazaphosphorin-4-one [31, 32], intensive studies of the six-membered ring systems containing benzdiazaphosphorinanone and benzoxazaphosphorinanone skeletons have been carried out, mainly by our group [33, 34]. Starting from the key precursors, the P-Cl species, i.g. 5,6-benzo-2-chloro-1,3,2-diazaphosphorinan-4-one or 5,6-benzo-2-chloro-1,3,2-oxazaphosphorinan-4-one, six-membered heterocyclic phosphazane systems **A**-**D** of different kinds, and some polyheterocylic benzdiazaphosphorinanones systems of type **E** have been synthesized.



A **B** **C**

D **E**

R, R^1 , R^2 = halogen, alkyl, arylorganylamino subsituents

All the heterocycles **A-E** exhibit chemical properties similar to their acyclic species. By oxidation of **C**, for example with oxygen or sulfur a series of phosphoryl derivatives **F** was obtained. Other oxidants hexafluoroacetone (HFA), e.g. or tetrachloro-orthobenzoquinone (TOB) have been used in the study of the oxidation of **A-E**. As reported, both TOB and HFA undergo oxidative addition to the $\sigma^3\lambda^3$-phosphorus atom to give the corresponding phosphoranes of type **G** and **H**. Some unusual ring-enlargement reaction have been observed during the oxidation of **A-C** with HFA [33, 34]. The phosphorus atoms exhibit complexation properties towards transition metals, e.g. Pt, Mo, Au, and give the corresponding complexes of type **I** upon coordination [33, 34]. Hydrolysis of P-Cl-derivatives and some phosphinan gave the phosphoryl compounds containing the P(:O)H unit with the six-mebmered ring unchanged [34].

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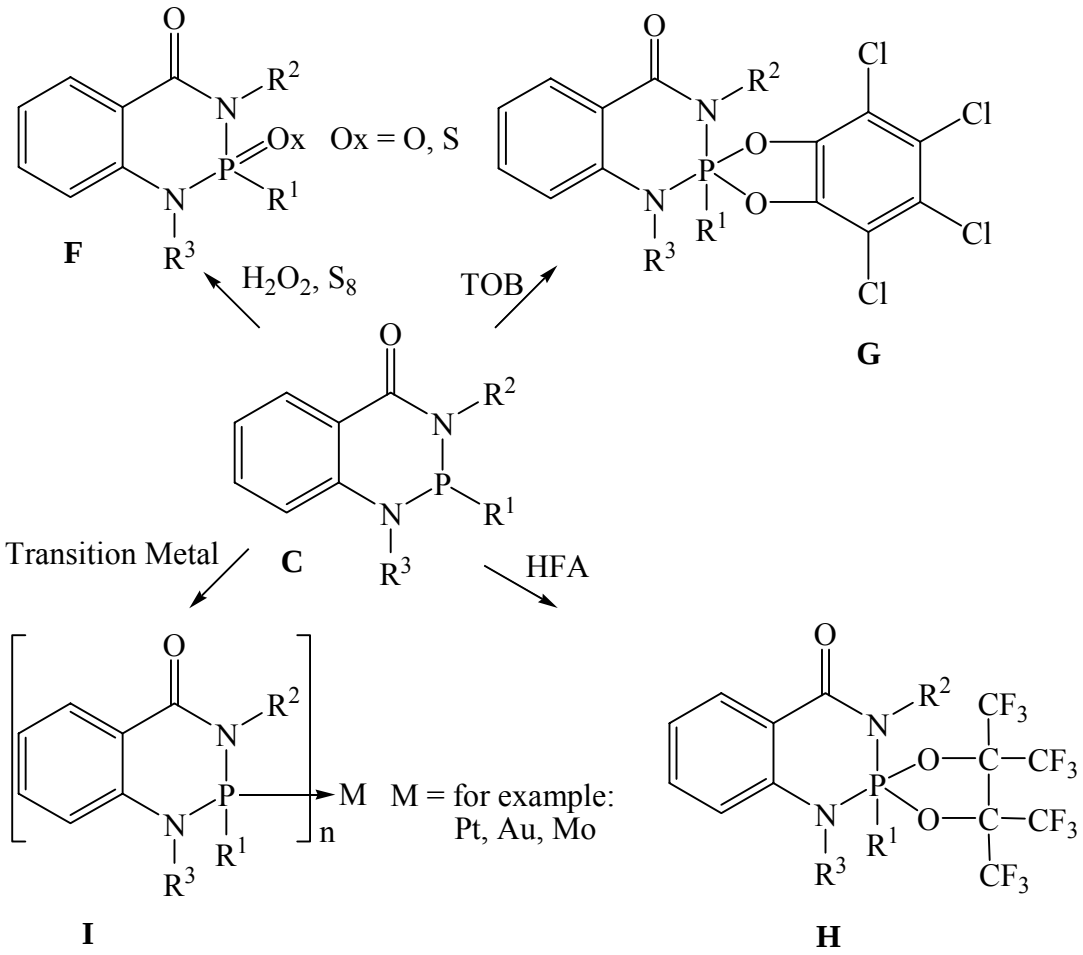


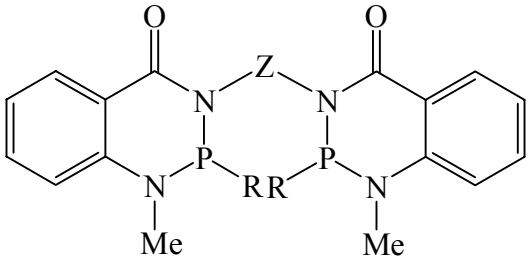
R^1, R^2, R^3= halogen, diorganylamino subsituents
alkyl, aryl

1.4.2. Bidentate Benzdiazaphosphorinanones and Benzoxazaphosphorinanones

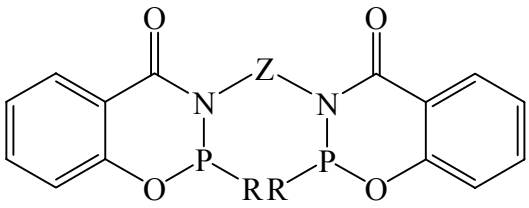
Bidentate phosphine ligands have been widely studied owing to their importance in a variety of applications, including organic synthesis and industrial catalytic processes [35, 36]. Unlike these traditional bidentate ligands with organic backbones, such as 1,2-(bis)diphenylphosphinoethane (DPPE), 1,8-(bis)diphenylphosphinonaphthalene (DPPA), which have been studied most intensively in the past decades with regard to coordination and catalysis, bis-heterocyclic phosphorus ligands have been explored to a much lesser extent.

Linked heterocyclic phosphazanes, for example, with two P-N units may exhibit interesting coordination properties both to transition metals and main group metals, considering the two soft base donor (P atoms) and the two hard base donor (N atoms). Recently, we have

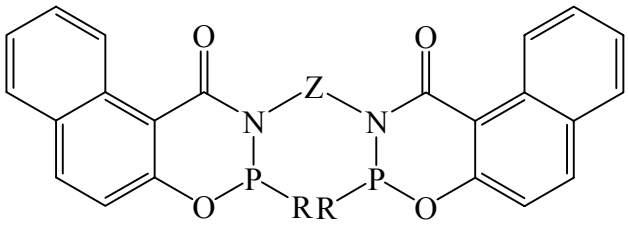
successfully synthesized the alkylene-linked 2-chloro-(1,3,2-benzdiazaphosphorinanone) systems by introducing an aliphatic alkylene bridging unit between two heterocyclic six-membered rings . Starting from the corresponding bis-amide, the bis-PCl derivatives can easily be prepared by reaction with PCl_3 in high yield. Aminolysis of these very reactive compounds readily gave the linked diphosphorus(III) compounds, with two heterocyclic phosphazane groups. In continuation of our research, we were interested in the linked heterocyclic systems containing two six-membered phosphorinanone heterocycles **J** , **K** and **L** .



J



K



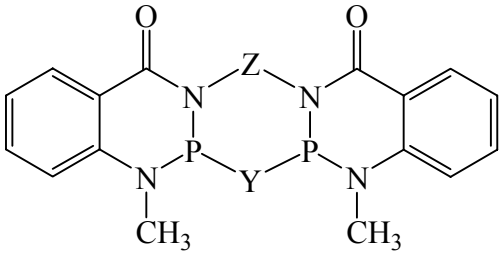
L

Z = CH_2CH_2, $CH_2CH_2CH_2$
R = Alkyl, aryl, halogen, diorganylamino subsituents

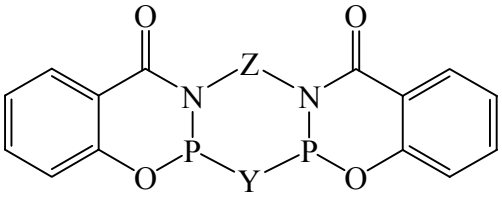
Special properties can be expected for the linked ring systems due to the two phosphorus atoms, which can readily form inorganic ring systems with different transitional metals. Furthermore, the bidentate ligands should show special stereic properties due to the two cyclic phosphorus-containing rings. Apart from the chemical properties, many P-N containing compounds have potential use in the pharmaceutical applications, as antitumor agents [37, 38].

1.4.3. Polycyclic Benzdiazaphosphorinanones and Benzoxazaphosphhorinanones.

Linked systems of type **J**, **K** and **L** have two phosphorus(III) coordination centers and thus are potential precursors for the synthesis of larger ring systems, **M** and **N**. The PCl-derivatives of **J**, **K** and **L** are especially important since the two active PCl groups can be employed in the ring closure reactions to give a series of cyclic compounds, with the ring-size depending on the other component used for the reaction. In addition, bidentate species of **J**, **K** and **L** should show interesting properties, especially in coordination chemistry. They can bind transition metals in a η^2 mode forming ring systems including transition metals as ring-element. By oxidation of the P(III) ring system with O and S containing two P=S or P=O groups, can be obtained, which again can be used as potentially selective ligands for ion recognition. The crown-like architecture of the molecules can be used as host for small molecules, taking advantage of inter-and/or intramolecular hydrogen bonding as driving force. It is known that in the polycyclic systems, ring size is critical [39, 40]. It is of interest to investigate the influence of the ring size on the chemical and physical properties of the polycyclic system. The following chapters deal with the investigations in this respect.



M



N

Z = CH_2CH_2, $CH_2CH_2CH_2$

Y = OCH_2CH_2O, OC_6H_4O, $OC_{10}H_6O$
Or Pt, Mo,

2. Synthesis of Linked Phosphorus-Containing Heterocyclic Systems

2.1. Introduction

Undoubtedly, the traditional bidentate phosphine ligands have dominated in the past decades in the field of coordination chemistry, catalysis and other applications [41, 42] (Fig.1). Many of these bidentate phosphines are air stable, and are available commercially. In contrast, P, N ligands are all air sensitive. The fact that bidentate P,N ligands have been largely unexplored in the same area as catalyst can be partially attributed to the lower stability, due to the weakness of the P, N bond. Another reason is the lack of a unique synthesis route.

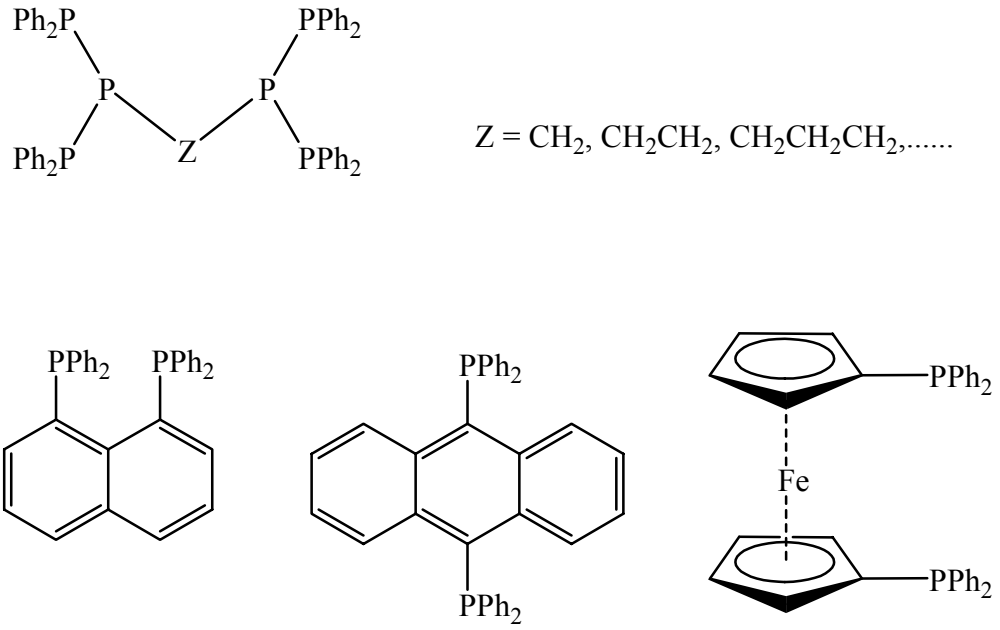


Fig.1. Bidentate Ligands with organic backbones containing phosphorus coordination centers.

A number of bidentate phosphines with inorganic backbones have been reported [19, 20, 43]. Heteroatoms such as N or Si, and other spacers have been chosen for linking two phosphine units (Fig.2). Nitrogen-linked diphosphines (or diphosphinoamine) are one of the most intensively investigated compounds. With two phosphorus atom chelating metal centers such as Pd, Pt, Ru, Cu, Zn, nitrogen-linked diphosphines can form various four-membered ring systems. In addition, the nitrogen atom linking two phosphorus atoms can also be employed

as a coordination center for main group alkali-metals such as lithium or potassium. Several reviews have covered this area [28, 44].

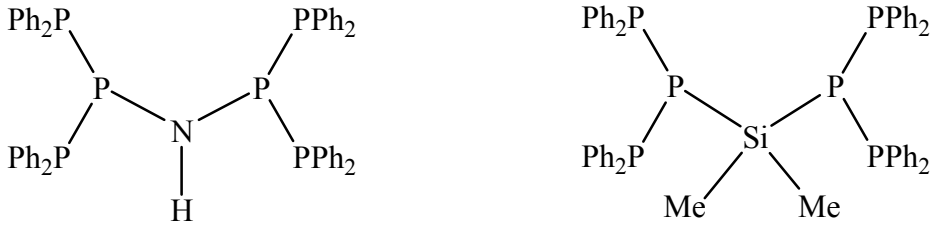
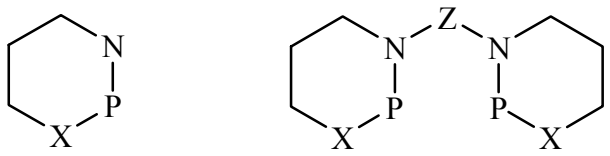


Fig. 2. Bidentate Ligands containing phosphorus coordination centers with inorganic backbones.

In contrast to the traditional bisphosphines with organic and inorganic backbones, bis-heterocyclic phosphorus ligands have received less attention, although many simple heterocyclic phosphorus-containing ring systems have been known. Linked heterocyclic aminophosphines, e.g. with two P(III)-N units may confer interesting coordination properties both on transition metals and main group metals, considering the two soft donor centers (P) and the two hard donor centers (N). Utilising the donor functionality of the P and N atoms, versatile heterocyclic systems containing transition metals can be prepared. Larger inorganic ring systems may be formed by ring closure, from the two phosphorus atoms with a platinum atom. In the past, we reported a series of 6-membered heterocyclic ring systems **A** [33, 34] including synthesis and structural studies. Linked systems of type **B** including their coordination chemistry with transition metals have also been reported recently [34].



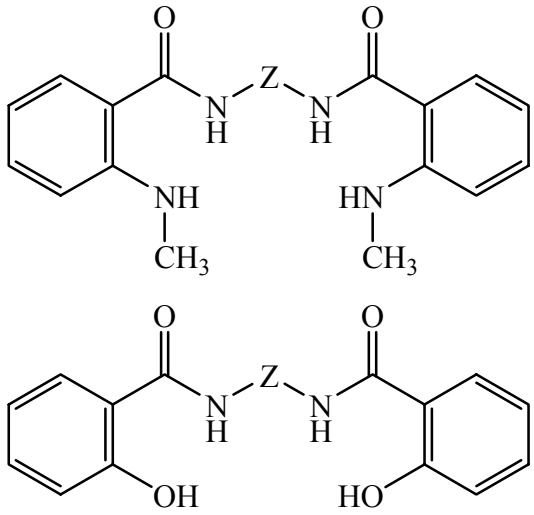
A **B**

Fig. 3. Mono-and Linked heterocyclic systems, X = O, N

In continuation of our research on designing and exploring new phosphorus-based heterocyclic ligands, we were interested in the new linked heterocyclic systems containing two six-membered phosphorinanone heterocycles.

2.2 Synthesis of bis-amides

Before the synthesis of phosphorus-containing heterocycles, our work has focused on the design and synthesis of a series of bis-amides with two active NH and OH groups, linked by an organic spacer (Fig. 4), which can be converted into the bis-PCl species by ring-closure via the reaction with PCl_3. A method has been developed that not only provides high yields of PCl-species in good purity but also permits simple isolation procedures. With two active P-Cl group in one molecule, this kind of bis-PCl species can serve as key precursor for the synthesis of bidentate ligands, they can also be used as components for the synthesis of phosphorus-containg macrocylic systems. For this purpose, the bis-amides **1-4** have been prepared following the literature method [45].

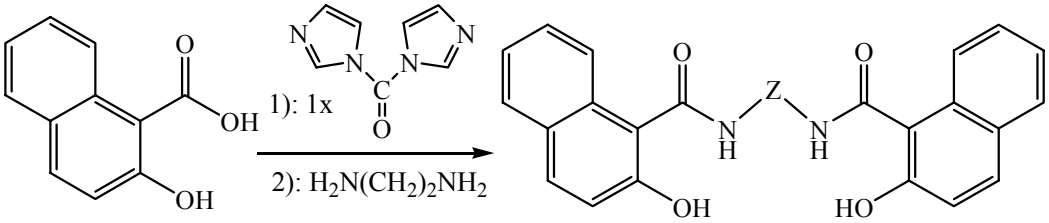


1: Z = CH_2CH_2
2: Z = $CH_2CH_2CH_2$

3: Z = CH_2CH_2
4: Z = $CH_2CH_2CH_2$

Fig. 4. Bis-amide systems

The new bis-amide **5** can readily be prepared, using the well established method of condensation of the naphthol with ethylendiamine in the presence of carbonyl diimidazole [45]. The reaction is clean, and the product is obtained in high yield (Eqn. 1).



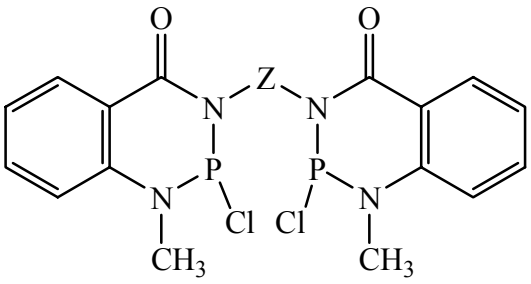
5: Z = CH_2CH_2 (1)

Compound **5** is a white powder which is not well soluble in common solvents such as methanol, dichloromethane, chloromethane, tetrahydrofuran, toluene or diethyl ether. It is well soluble in dimethyl sulfone (DMSO). The ^{1}H-NMR spectrum of **5** recorded in d6-DMSO shows that the resonances of the aromatic H occur between 7.74-7.12 ppm as several multiplets. The O*H* resonance lies at 8.24 ppm, the N*H* resonance at 3.36 ppm, both as singlet and are exchangeable with D_2O. The poor solubility of **5** may be explained by the formation of inter-molecular hydrogen bonds, which lead to the aggregation of the molecules via H–N···H or H–O···H hydrogen bonding.

2.3. Reaction of the Bis-amides with PCl_3, Preparation of the Bis-PCl Derivatives 6-10

Chlorophosphines, in general are valuable starting materials for P-C, P-N, or P-P coupling reactions. Since the P-Cl bond is weak, so that chlorophosphines can be transformed into a wide range of phosphines, many of which are important ligands in coordination chemistry. Therefore, design and synthesis of chlorophosphines is one of the most important and most challenging part in organophosphorus chemistry. Since most of the chlorophosphines are air sensitive, some of them are generated only in *situ*. Separation and further handling or work-up requires special skills and all operations must be completed in an inert atmosphere. On exposure to moisture, the chlorophosphine R_2PCl (R = alkyl, aryl, or organoamino groups) readily gave the hydrolysis product, by exchange of Cl with OH forming R_2P-OH, which in most cases rearranges to $R_2P(:O)H$ species.

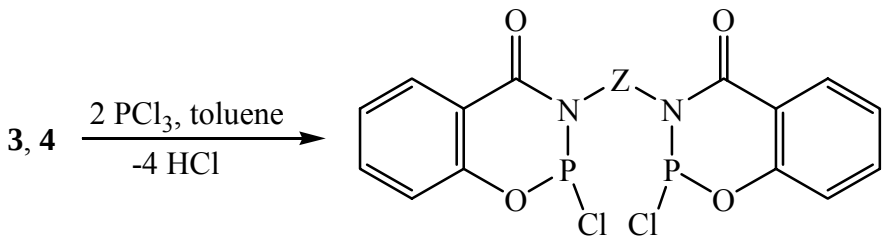
For the synthesis of the bis-PCl species **6** and **7** it is reasonable to react PCl_3 with the bis-amide, **1** and **2**. Indeed, the reaction of **1** and **2** with two equivalents of PCl_3 gave the desired bis-PCl derivatives **6** and **7** in high yield (Fig.5). The reaction took place in refluxing toluene and the liberated HCl was removed by a light steam of dry nitrogen, so that no additional base was needed to trap the HCl. Other solvents such as THF or dichloromethane can also be used, but longer reaction times are required.



6: Z = CH_2CH_2
7: Z = $CH_2CH_2CH_2$

Fig. 5. Symmetrical Bis-PCl systems

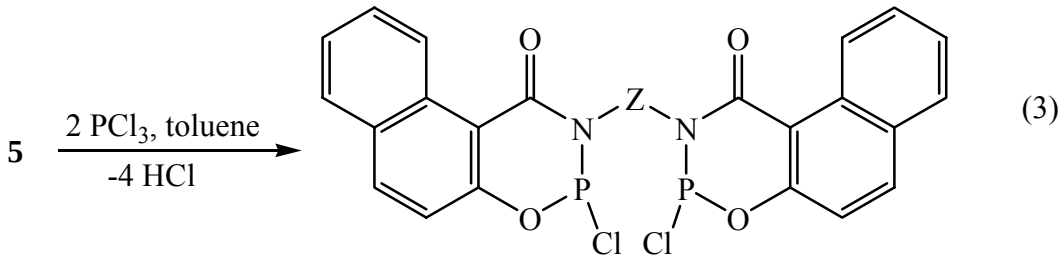
The same literature method is employed for the preparation of the bis-PCl species **8** and **9**, as shown in Eqn.2. Using toluene as a solvent, **8** and **9** can be obtained in near quantitative yield. The ring-closure reaction forming **8** and **9** is, surprisingly highly selective, despite the presence of two NH and two OH groups. The reaction mixture of **3** with PCl_3 e.g. displays only one singlet at 143.7 ppm in the ^{31}P NMR indicating that only **8** is formed during the reaction. The same results were obtained from the reaction of **4** with PCl_3. No evidence of intermolecular reactions which could lead to the formation of polymers or higher oligomers could be observed. Removal of the solvent gave the product as a white solid, which can be used for the next step without further purification. The reaction of **3** and **4** with PCl_3 at room temperature in dichloromethane in the presence of triethylamine gave the same product, however the overall yield was lower than by directly heating the mixture of **3** or **4** and PCl_3. Furthermore, the purification process is more difficult. Beside the main product, triethylamine hydrochloride is also formed. Since the PCl species **8** and **9** are not well soluble in ether or toluene, the separation of the desired compounds from triethylamine hydrochloride salts is more complicated.



(2)

8: Z = CH_2CH_2
9: Z = $CH_2CH_2CH_2$

Under the same conditions, the bis-PCl derivative **10** was prepared according to Eqn. 3. The reaction took place smoothly in refluxing toluene with HCl being liberated simply by heating. The yield is nearly quantitative.



(3)

10: Z = CH_2CH_2

Although all the bis-PCl derivatives **8-10** derivatives display one signal in the ^{31}P NMR spectra in toluene asa reaction medium, in dichloromethane the signals became slightly broader. The compounds may exist in a mixture of two or more rotamers, due to the higher polaritiy of dichloromethane. This phenomenon is in accordance with our previous observation [34c]. The ^{31}P chemical shift of **8**, **9** and **10** are only marginally different, suggesting that the structural variation does not significantly alter the values of the ^{31}P chemical shift. They lie at slightly higher frequency than those of **6** and **7** due to the more electron-withdrawing effect of oxygen, compared to nitrogen. In the ^{1}H NMR spectra, **8-10** show multiplets at 6.7-8.6 ppm for the aromatic hydrogen. In the EI-MS spectra of compounds **8-10** only low intensity-molecular ions could be observed. The main fragments result from the hydrolysis products. As most chlorophosphine compounds, all the PCl-species **8-10** are very air-sensitive and decompose on exposure to moisture to give the corresponding P(:O)H compounds, as indicated by signals at about 0 ppm in the ^{31}P NMR spectra, with a high $^{1}J(PH)$ value at about 600 Hz, typical of P(:O)H species [46].

2.4. Synthesis of Bidentate Ligands

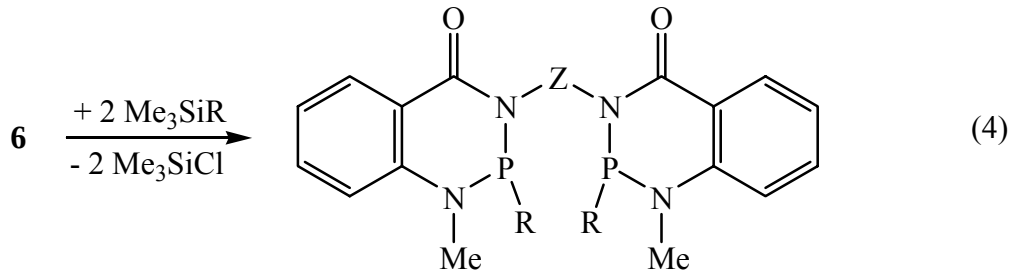
2.4.1. General routes for the formation of the P-N bond.

In general, P−N coupling follows a similar strategy as that used in C−C coupling in organic chemistry, although the scope of the related P-N chemistry is often limited by the comparative weakness of the P−N bond.

Starting from chlorophosphines, several methods have been developed and many have became standard for the synthesis of new aminophosphines. Besides the commonly used aminolysis method, an alternative, sometimes more convenient synthetic route for the preparation of aminophosphine is to treat the chlorophosphine with trimethylsilyamine, (R_2NSiMe_3). Since the -$SiMe_3$ unit is a very good leaving group under slightly acidic conditions provided by the chlorophosphine, aminophosphines can easily be obtained with elimination of Me_3SiCl. The latter is a liquid of low boiling point, so that it can readily be removed by distillation. The reaction can be kinetically controlled by choosing the solvent, and the progress of the reaction can be monitored using ^{31}P NMR spectrum. This method using trimethylsilyamine is more expensive, and sometimes use is limited due to the lack of the availability of the starting material R_2NSiMe_3. However, the method often provides high yields of aminophosphines, and the reaction is often selective.

2.4.2. Synthesis of bidentate ligands

It is our experience that the target compounds, the PCl derivatives, are usually not well soluble in diethyl ether, and we chose the route starting from the trimethylsilyamine, in order to avoid the formation of triethylamine hydrochloride, and the inconvenience of the separation of the triethylamine hydrochloride. Compounds **11** and **12** were thus prepared according to the Eqn. 4. The reaction took place spontaneously in dichloromethane at room temperature. Other solvents such as diethyl ether or thf can also be used. After removal of the solvent and the volatile Me_3SiCl the product was obtained in high yield.

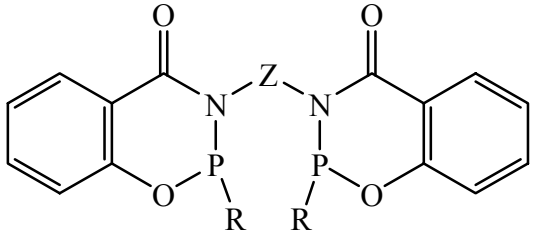


(4)

11: R = NMe_2, Z = CH_2CH_2

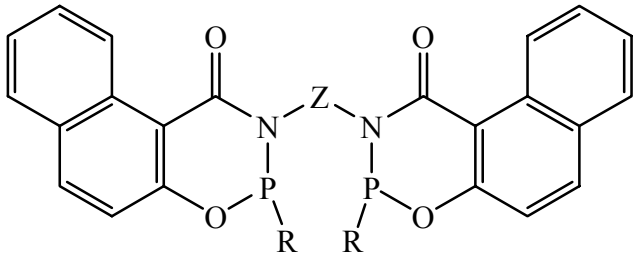
12: R = $N(CH_2CH_2)_2O$, Z = CH_2CH_2

Similarly, compound **13** was prepared according to Eqn. 5. **8** was initially only slightly soluble in dichloromethane at room temperature, and formed a milky suspension upon cooling. After the addition of trimethylsilyamine, the solution turned clear immediately. The ^{31}P NMR spectrum showed that the reaction was complete within less than 30 min at room temperature.

8 $\xrightarrow[- 2\ Me_3SiCl]{+ 2\ Me_3SiR}$  (5)

13: R = $N(CH_2CH_2)_2O$, Z = CH_2CH_2

Compounds **14-17** were prepared similarly in near quantitative yield, according to Eqn. 6. There is no significant influence of the additional two phenyl groups on the reaction process. **14-17** are all stable in the solid state in the air, but decompose back to the bis-amides if the solutions are exposed to moisture.

10 $\xrightarrow[- 2\ Me_3SiCl]{+ 2\ Me_3SiR}$  (6)

14: R = NMe_2, Z = CH_2CH_2

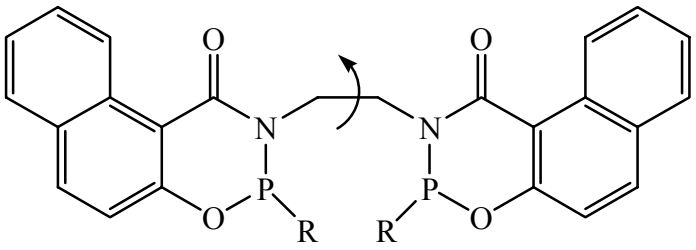
15: R = NEt_2, Z = CH_2CH_2

16: R = $N(CH_2CH_2)_2O$, Z = CH_2CH_2

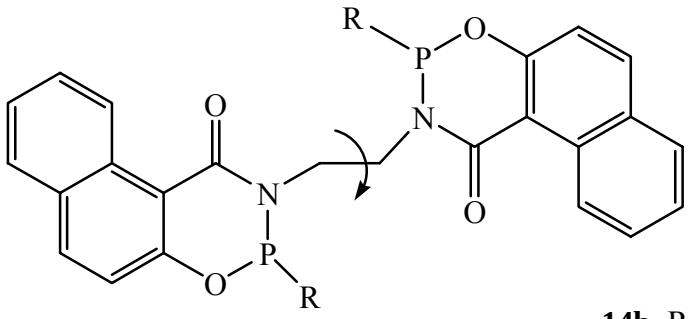
17: R = NHPh, Z = CH_2CH_2

In solution, **14-17** display two signals in the ^{31}P NMR spectra with very close chemical shift and nearly equal intensity at r.t. There have been studies about the isomerization of the bis-amides, and similar results have been observed [45]. Due to the introduction of the phosphorus-containing group, the molecules are more bulky, and one isomer could prevail, due to steric hinderance caused by the substituent at phosphorus. However, due to the possible rotation around the C-C bond in the bridging unit, or rotation around the P-C bond,

two or more isomers may exist in equibrilium in the solution. We speculate that the rotamerization is induced, most likely by the rotation of the C-C bond in the bridging unit, as illustrated below.



14a, R = $N(CH_3)_2$



14b, R = $N(CH_3)_2$

Rotations around P and the R group, attached to phosphorus cannot be ruled out. Attempts to separate one single isomer were in all cases unsuccessful.

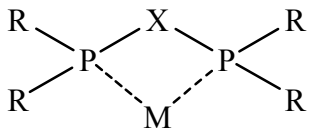
The reaction of the bis-PCl precursor **10** with bis/trimethylsilyl)oxalate (Me_3Si-C(:O)C(:O)-$SiMe_3$) under similar conditions gave a powder which insoluble in commen solvents such as dichloromethane, chloroform, acetonitrile, toluene, allowing no comments on the outcome of the reactions.

3: Complexation and Oxidation of Bisaminophosphine Systems

3.1. Introduction:

Many compounds of three-coordinated phosphorus can readily be oxidized in the air to give phosphine oxides, involving four-coordinated phosphorus [cross-ref]. Among organophosphines, arylphosphines and alkylphosphines with bulky groups are more or less air stable. Aminophosphines are usually more reactive, and can readily react with water to give the appropriate hydrolysis products. In contrast, compounds of four-coordinated phosphorus, such as phosphine oxides, or phosphonium salts are more stable [47] and some will survive treatment with strong bases such as Grignard agent [48]. Phosphorus-containing compounds that have industrial applications almost all involve four-coordinated phosphorus, and they are usually present as phosphonium salts or phosphoryl species. Complexes formed by three-coordinated phosphorus compounds are also stable, and have widely been used as catalysts in many reactions [41, 49, 50].

The traditional coordination chemistry displayed by neutral aminophosphines involves bonding via the phosphorus centre only. Among aminophosphines, bidentate aminophosphines can serve as rigid ligands which give rise to interesting ring systems.



R = Aryl, alkyl groups,
X = N, $Si(CH_3)_2$,
M = Pd, Pt,

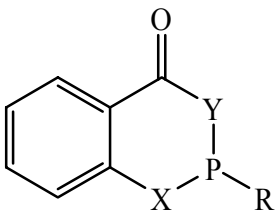
The major application of transition metal complexes containing phosphine ligands is in homogeneous catalysis. Since Wilkinson's work on the catalytic activity of $Rh(PPh_3)_3Cl$ for hydrogenation reactions [51], phosphine complexes have extensively been developed, and are now commonly in use in carbonylation, hydroformation, isomerisation, and other organic syntheses [49-51].

Compared to the vast body of data accumulated for bisphosphines containing carbon backbones there has been very little coverage of aminophosphine complexes. The relative weakness of the P-N bond may be one reason why this area is largely unexplored. Recent developments in exploring aminophosphine complexes as ligands in active catalysts in a

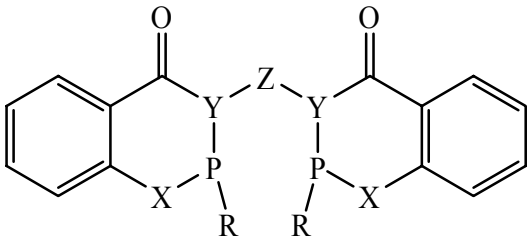
number common reactions are certainly very encouraging [28, 52]. It is not unreasonable to expect that this trend will continue.

Due to the higher stability of P(IV) and P(V) compounds compared to P(III) compounds, many application studies can be conducted. For example, phosphine sulphide or oxide can be employed as chemsensors [53]. It is well known that oxidation of tertiary phosphines e.g. with H_2O_2, elemental sulfur or selenium gives phosphine chalcogenides $R^1R^2R^3P{=}X$ (R^1, R^2, R^3 = Alkyl, Aryl; X = O, S, Se). Other oxidizing agents like hexafluoroaceton (HFA) and tetrachlororthobenzochinon (TOB) can undergo oxidative addition reaction with phosphines to afford P(V) species.

Recently, the synthesis of a series of the six-membered heterocyclic ring systems **A** and **B** was reported [33, 34]. The synthesis of similar alkylene-linked (1,3,2-benzdiazaphosphorinanone) systems and their coordination chemistry with some transition metals were also disclosed recently [34]. It was found that the reactivity of these species is strongly dependent on the molecular structure, which is different in the environment of the phosphorus atom and the length of the bridging units.



A



B

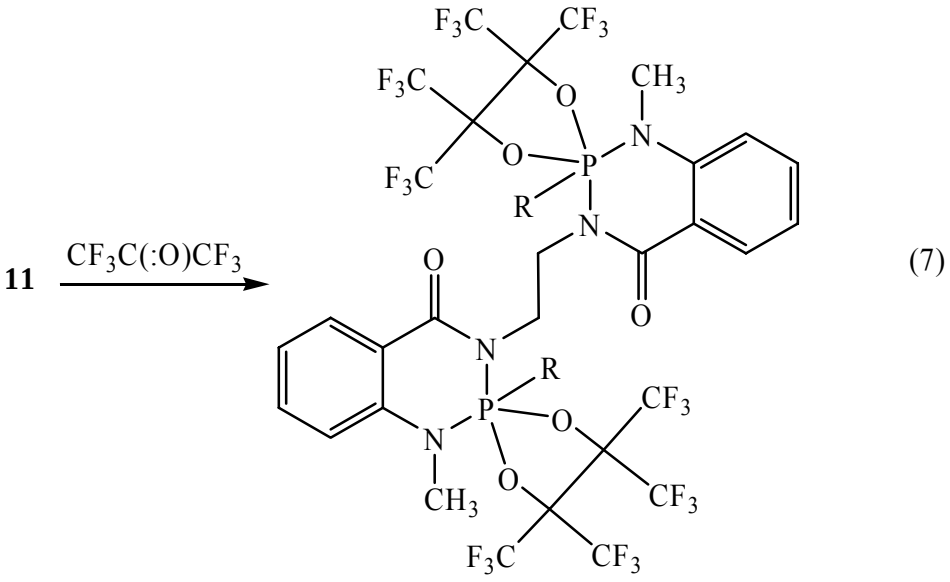
X , Y = O, NR; Z = $(CH_2)_n$,

With these compounds in hand, we were interested in their reactivity towards oxidizing agents such as hexafluoroaceton (HFA) and tetrachlororthobenzochinon (TOB) and towards several transition metal complexes.

3.2. Reaction of Compounds 11-17 with Hexafluoroaceton (HFA) and Tetrachlororthobenzochinon (TOB)

Oxidative addition of carbonyl compounds (e.g. $CF_3C(:O)CF_3$, $CF_3C(:O)CH_3$) to P(III) species is a widely used synthetic pathway to generate P(V) compounds [54] . α-Dicarbonyl compounds such as TOB were also found to be good oxidative agents for three-coordinate phosphines [55]. Oxidative addition reactions of phosphorinanone with HFA and TOB have extensively been investigated [33].

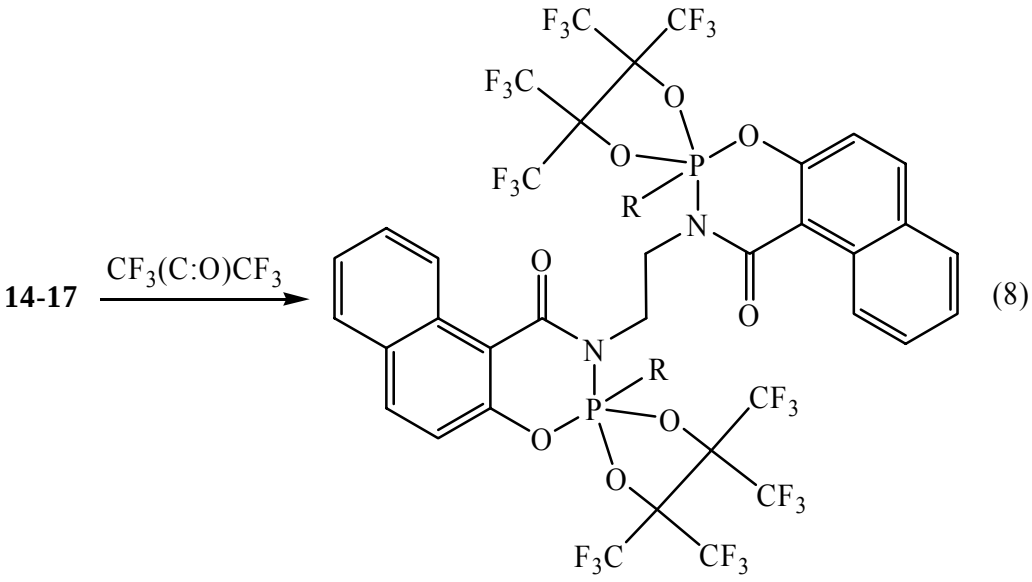
Reaction of ligand **11** with HFA gave new compounds **18** according to Eqn. 7.



(7)

18: R = $N(CH_3)_2$

When compounds **14-17** were allowed to react with excess HFA in dichloromethane, the $\sigma^5\lambda^5$P-oxazaphosphorinanones **19-22** were obtained.



(8)

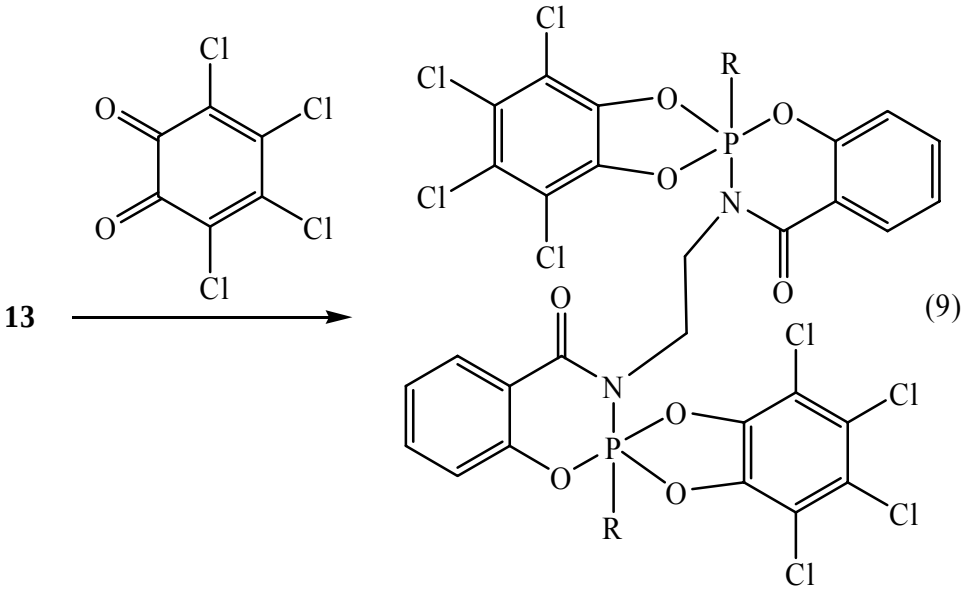
19: R = $N(CH_3)_2$

20: R = $N(CH_2CH_3)_2$

21: R = $N(CH_2CH_2)_2O$

22: R = NHPh

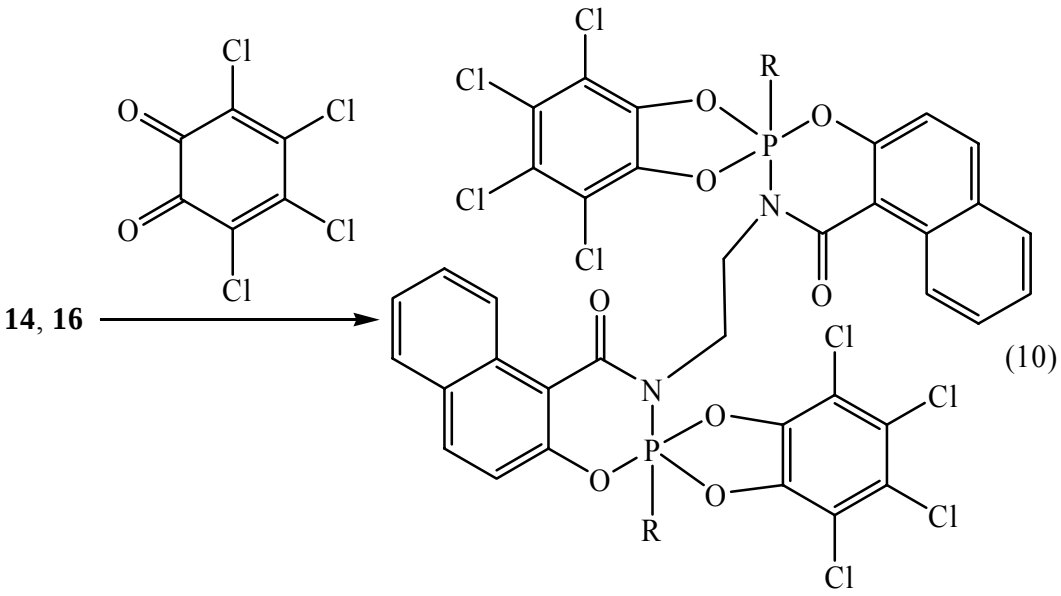
Compound **23** was prepared from **13** and TOB in high yield.



(9)

23: R = $N(CH_2CH_2)_2O$

Similarly, the $\sigma^5\lambda^5$P-oxazaphosphorinanones **24** and **25** were prepared from **14** and **16** by the oxidative addition of TOB at room temperature to the corresponding $\sigma^3\lambda^3$P-precursors in dichloromethane (Eqn.10).



24: R = $N(CH_3)_3$
25: R = $N(CH_2CH_2)_2O$

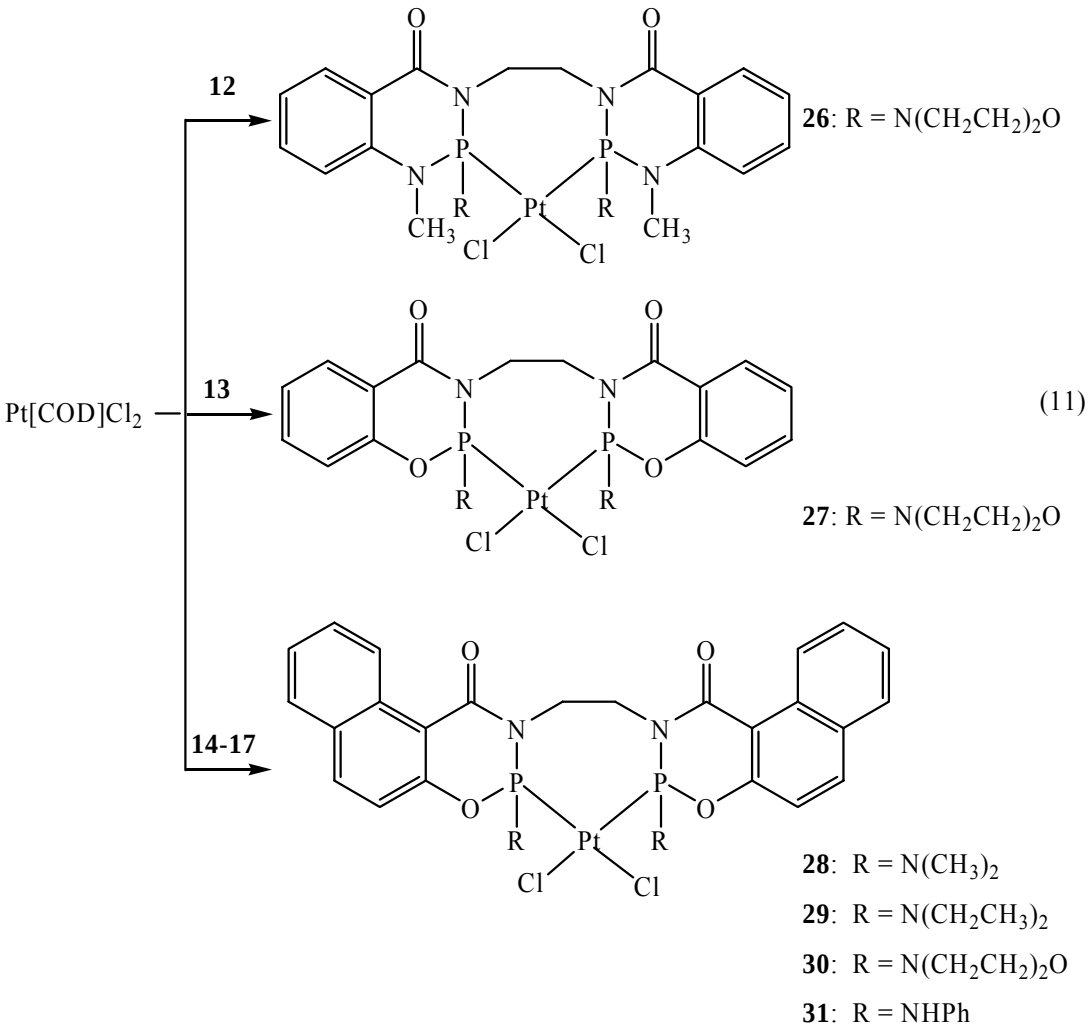
The phosphorinanones **18-25**, involving $\sigma^5\lambda^5$P, all show two signals in the ^{31}P-NMR spectra in the expected region, typical of this kind of compound. However, it was found that compounds **20** and **22** display only one sharp ^{31}P signal, respectively, even after a long acquisition time. The δ (^{31}P) values of **19**, **20**, **21** and **22** are only slightly different (43.2-47.8 ppm). The different substituents at the central phosphorus atom seem to have only a minimal effect on the ^{31}P values of the $\sigma^5\lambda^5$P-oxazaphosphorinanones. The solubility of all the compounds were so poor, and it was impossible to conduct more detailed NMR studies, in order to investigate the stereochemistry of the molecules. For most of the compounds, no meaningful ^{13}C-NMR spectra could be obtained. Even ^{1}H-NMR spectra were not well resolved. Hence, the mass spectra remain the most useful method of compound identification. In each case, the molecular ion was seen in the EI-MS spectra of **18-25**. Attempts to separate the mixtures of products have, thus far, been successful only for **19**. Using dichloromethane as solvent, one conformer could be isolated by crystallization.

3.3. Reactions of Compounds 12-17 with $Pt[COD]Cl_2$(COD=1,5-Cyclooctadien), $[NBD]Mo(CO)_4$ (NBD = Norbornadien) and [THT]·AuCl (THT = Tetrahydrothiofen)

Platinum complexes have received increasingly interests due to their use in catalysis, and in pharmaceutical applications [56]: some cis-platinum complexes can have potentially applications as anti-cancer drugs [57].

3.3.1. Reaction of 12-17 with $Pt[COD]Cl_2$

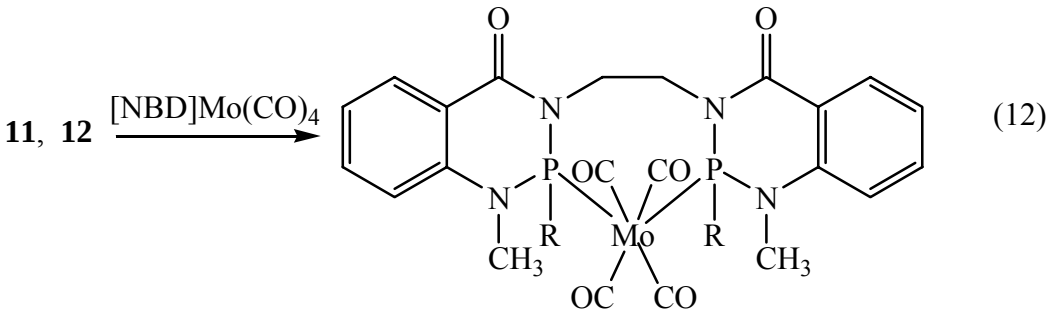
The reaction of the bidentate compounds, **12-17** with $Pt[COD]Cl_2$ (COD = 1,5-Cyclooctadien) in dichloromethane gave rise to the new complexes, **26-31**. The two phosphorus atoms of the ligands form, together with the platinum atom, the new 7-membered ring systems $[(PNCH_2CH_2NP)Pt]$. Compound **28** exists as a single isomer, as suggested by a sharp singlet in the ^{31}P-NMR spectrum in the solution of $CDCl_3$. However, in the reaction mixtures of **29** and **30**, two signals with very similar $\delta(^{31}P)$ values were observed. It is thought that two isomers are present in solution. By recrystallazation from dichloromethane one isomer of **30** could be isolated. The value of $^{1}J(PPt)$ in **26-31** of the order of about 2600 Hz indicates that the two chlorine atoms are in *cis* position, which is confirmed in the cases of **28** and **30** by X-ray structure determination (see section **3.3.3.** on page 29)



(11)

3.3.2. Reaction of 11 and 12 with [NBD]Mo(CO)$_4$ (NBD = Norbornadien) and [THT]·AuCl (THT = Tetrahydrothiofen)

The reaction of the bidentate ligands with [NBD]Mo(CO)$_4$ in dichloromethane gave the complexes **32** and **33** in high yield. Compound **32** displays two signals at 149.3 and 147.3 ppm in the ^{31}P NMR spectra in $CDCl_3$ at room temperature, while **33** shows one signal at 147.7 ppm. Both compounds show intensive molecular peaks in the EI-MS spectra. However, due to the poor solubility of the two compounds, detailed NMR data could not be obtained, allowing no further comments on the structure.

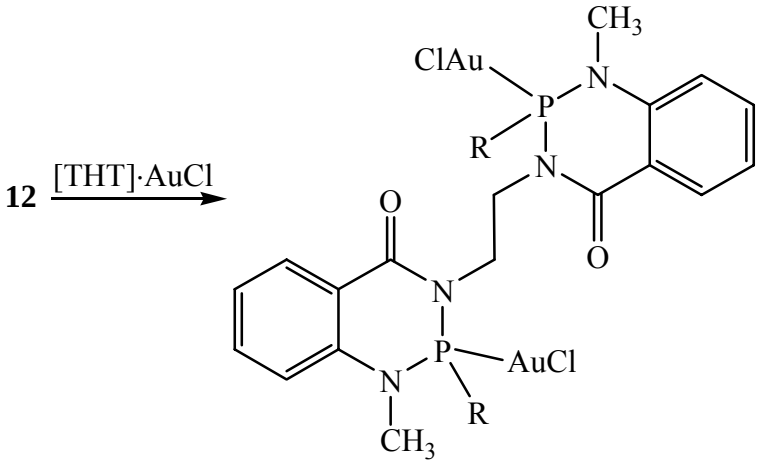


(12)

32: R = $N(CH_3)_2$

33: R = $N(CH_2CH_2)_2O$

The reaction of **12** with [THT]·AuCl gave **34**. **34** was found to display two signals at 93.9 and 93.2 ppm with approximately equal intensity in the ^{31}P-NMR spectra in $CDCl_3$ at room temperature, indicating two isomers existing in solution. However, attempts on recrystallization resulted in the formation of free ligand **12** and a black powder, which clearly originated from the decomposition of the complex, with formation of elemental gold.



(13)

34: R = $N(CH_2CH_2)_2O$

3.3.3. Crystal and Molecular Structure of 19, 28 and 30

Compound **19** crystallizes with a crystallographic inversion centre in the middle of the bridging ethylene group, C12-C12'. The torsion angle N1-C12-C12'-N1' is thus 180°, and the two naphthyl groups are parallel. The phosphorus and the nitrogen atom of the phosphorinanone heterocycle lie 104.4 and 39.1 pm on the same side of the best plane of the other four ring atoms (mean deviation: 1.1 pm). The atoms O4, P, O3 and C15 of the five-

membered ring are coplanar with a mean deviation of 2.8 pm, C18 lies 48.0 pm out of this plane. The geometry at phosphorus is distorted trigonal bipyramidal, whereby the axial atoms O1 and O4 subtend an angle of 170.7° at phosphorus.

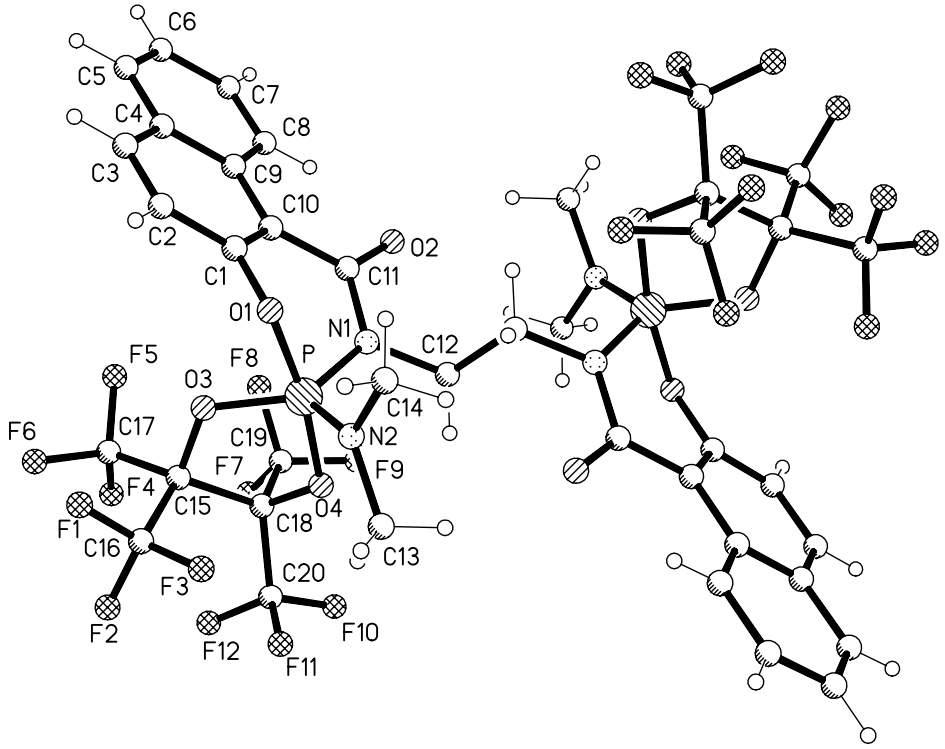


Fig.6: The formula unit of compound **19** in the crystal. Selected bond lengths [pm] and angles [°]: P-N2 162.1(3), P-O1 165.1(3), P-O3 166.4(3), P-N1 170.2(3), P-O4 172.8(3); N2-P-O1 93.33(14), N2-P-O3 126.42(14), O1-P-O3 84.56(13), N2-P-N1 114.40(15), O1-P-N1 92.80(13), O3-P-N1 119.18(13), N2-P-O4 92.42(14), O1-P-O4 170.71(12), O3-P-O4 86.15(12), N1-P-O4 91.47(13).

Because the compounds **28** and **30** differ chemically only in the substituents at N2 and N2', their structures are discussed together. Because of the complexation with platinum the two halves of the molecules are forced to the same orientation, whereby the two naphthyl groups subtend an angle of 34.6° (**28**) or 49.5° (**30**), with mean deviations from the best planes of 2.8 and 4.4 pm or 2.2 and 4.7 pm, respectively. The torsion angle of the bridging N1-C12-C12'-N1' unit is –37.7° (**28**) or 45.1° (**30**). It is noteworthy that in both molecules the distortion of the two phosphorinanone heterocycles differs significantly. If the rigid part O1-C1-C10-C11 or O1'-C1'-C10'-C11' is considered planar (mean deviations: 0.2 and 2.7 pm (**28**) or 0.6 and

2.6 pm (**30**)), the deviations of the phosphorus and nitrogen atom from one of these planes is much larger than from the other (106.1 (P) and 53.6 (N), 53.8 and 40.5 pm (**28**) or 105.6 (P) and 35.4 (N), 27.9 and 30.5 pm (**30**)).

In both molecules the conformation of the seven-membered ring formed by platinum, the two complexing phosphorus atoms and the N1-C12-C12'-N1' bridge is almost the same. The arrangements at the phosphorus and nitrogen atoms are approximately planar (mean deviations: 8.6 (**28**) or 12.2 pm (**30**)), the platinum atoms lie 30.5 (**28**) or 33.2 pm (**30**) to one side of this plane, the carbon atoms 101.8 and 132.0 pm (**28**) or 133.5 and 93.2 pm (**30**) to the other. The platinum atoms lie 2.2 pm (**28**) or 6.0 pm (**30**) out of the best plane of their α-substituents (mean deviations: 0.4 or 8.8 pm); the significant distortion from planarity in **30** is reflected in the displacement of Cl1 by 34 pm from the plane of the other four atoms. Bond lengths at platinum can be considered normal. The Pt-P bonds show the usual shortening effect induced by electronegative substituents at phosphorus, as noted previously. In contrast, Pt-Cl bond lengths vary little in such complexes.

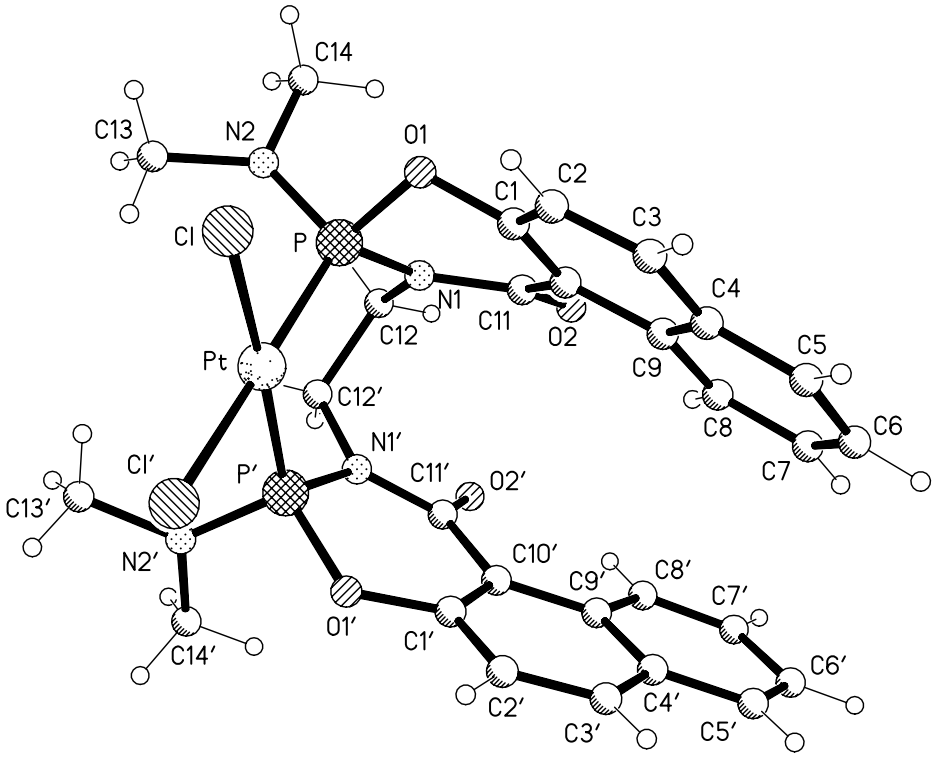


Fig.7: The formula unit of compound **28** in the crystal. Selected bond lengths [pm] and angles [°]: Pt-P' 220.42(4), Pt-P 221.44(4), Pt-Cl 235.10(4), Pt-Cl' 235.96(4), P-O1 160.97(12), P-N2 161.79(15), P-N1 169.54(14), P'-O1' 159.91(13), P'-N2' 161.79(14), P'-N1' 168.62(13); P'-Pt-P 98.298(15), P'-Pt-Cl 174.335(15), P-Pt-Cl 87.281(16), P'-Pt-Cl' 84.806(15), P-Pt-Cl' 176.612(14), Cl-Pt-Cl' 89.594(15), O1-P-N2 105.49(7), O1-P-N1 97.57(6), N2-P-N1 104.19(7), O1-P-Pt 111.09(4), N2-P-Pt 115.59(6), N1-P-Pt 120.60(5), O1'-P'-N2' 104.39(7), O1'-P'-N1' 99.47(6), N2'-P'-N1' 106.31(7), O1'-P'-Pt 112.44(5), N2'-P'-Pt 113.29(5), N1'-P'-Pt 119.16(5).

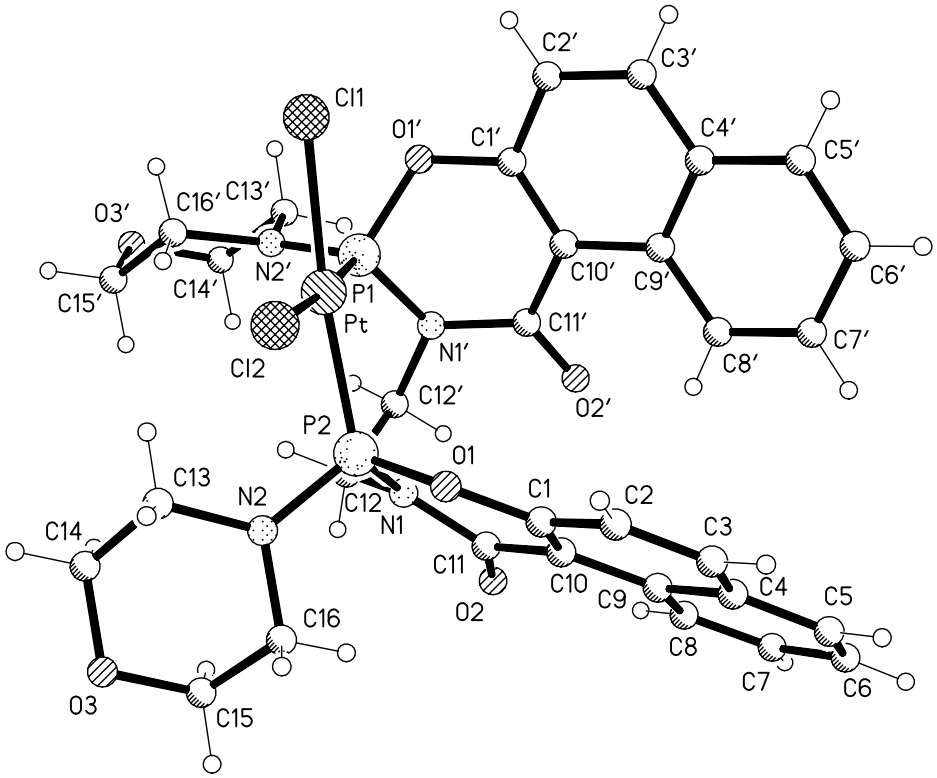


Fig.8: The formula unit of compound **30** in the crystal. Selected bond lengths [pm] and angles [°]: Pt-P 221.35(5), Pt-P’ 221.77(5), Pt-Cl 233.87(5), Pt-Cl’ 234.54(5), P’-O1' 161.75(15), P’-N2' 162.27(16), P’-N1' 168.82(17), P-O1 160.65(13), P-N2 162.95(17), P-N1 168.40(17); P-Pt-P’ 98.164(19), P-Pt-Cl 85.539(18), P’-Pt-Cl 176.121(19), P-Pt-Cl’ 170.280(17), P’-Pt-Cl’ 88.163(19), Cl-Pt-Cl’ 88.316(18), O1'-P’-N2' 105.39(8), O1'-P’-N1' 97.68(8), N2'-P’-N1' 104.40(8), O1'-P’-Pt 113.23(6), N2'-P’-Pt 115.64(6), N1'-P’-Pt 118.31(6), O1-P-N2 106.28(8), O1-P-N1 99.52(8), N2-P-N1 103.98(9), O1-P-Pt 109.33(6), N2-P-Pt 116.32(7), N1-P-Pt 119.48(7).

4. Phosphorus-containing Polycyclic Systems I

4.1. Introduction

Macrocycles are usually defined as a class of cyclic compounds with more than 8 atoms as part of the ring [58, 59]. Among the macrocyclic systems, crown ethers, or azacrown ethers are most common. Many of the crown ethers are commercially available and their application has extensively been investigated [60]. Macrocycles containing heteroatoms such as phosphorus, silicon, and sulfur have been known for a long time. The first ten-membered phosphorus-containing macrocycles of the phosphite type (acid and neutral) were obtained as early as 1897 by Stokes long before the discovery of crown ethers [61, 62], they have not been intensively studied; partially because of experimental difficulties, such as multistep procedures, low yields, and instability of the final products[63, 64]. However, due to the ever-growing interest in the application of phosphorus-containing macrocyclic species as ligands in transition metal-catalyzed in homogenous catalysis, chromatographic separation of metal ions, molecular recognition and biological applications, the design and synthesis of phosphorus-functionalised macrocycles have attracted increasing interest in the last decades [65, 66].

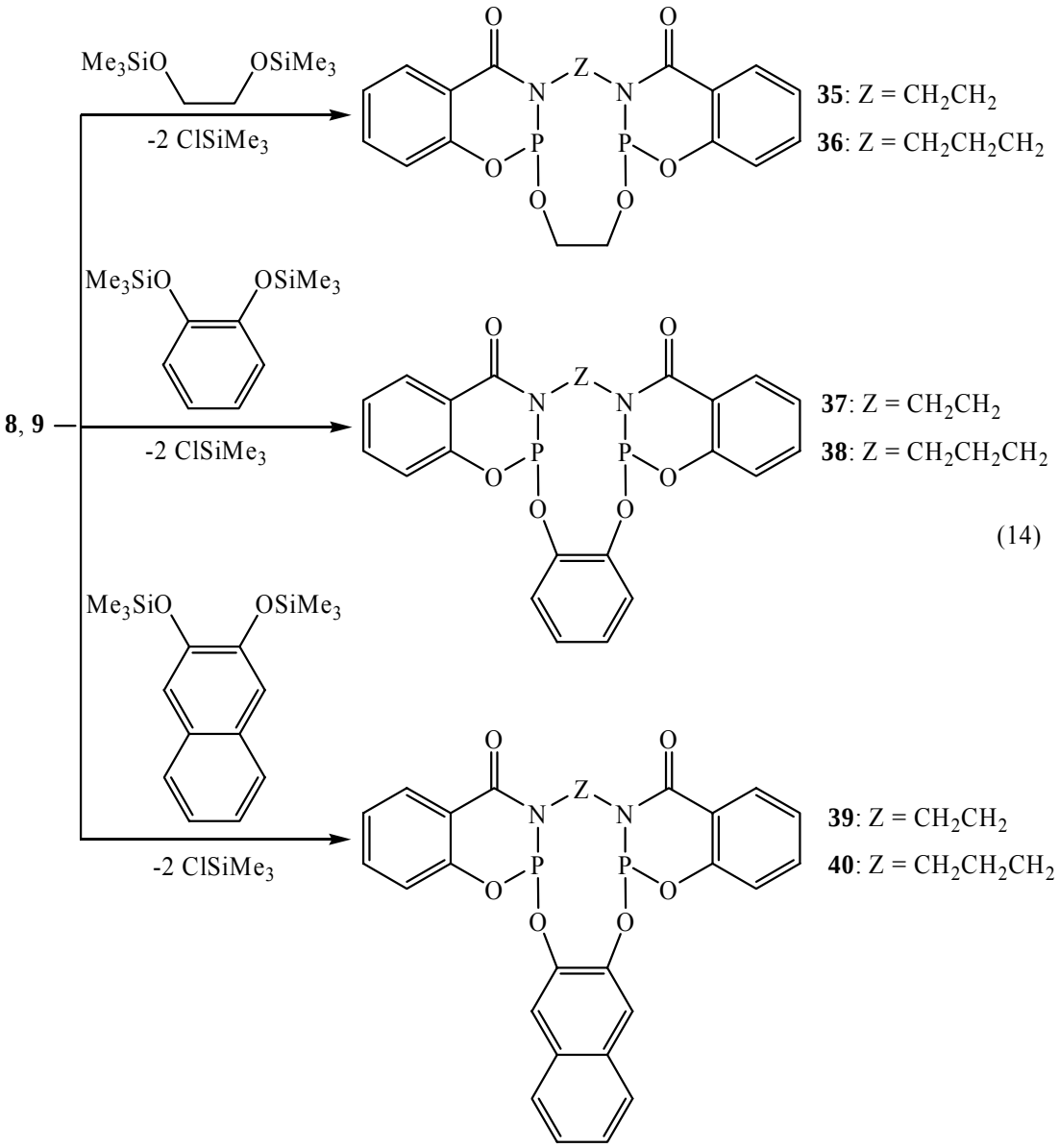
In the field of separation science, utilization of macrocyclic ligands for the determina-tion and separation of metal ions is receiving the ever-increasing attention of researchers. Ionophores with phosphorus-containing donor groups (phosphine oxide, phosphonate, phosphate, etc.) immobilized on a macrocyclic platform are of particular interest because the metal-binding properties of such ligands may integrate the selectivity of macrocycles and the efficiency of organophosphorus separation agents [67]. During the last two decades, several reviews concerned with the synthesis of phosphorus-containing crown ethers (CEs), lariat ethers (LEs), and cryptands have appeared [68]. The very recent survey were dedicated to the preparation of phosphorus-containing calixarenes [69] and their applications in separation [70].

One of the common methods to prepare macrocyclic systems is the cyclization of two or more components. This method usually requires high dilution conditions and in many cases template methods. Frequently, the yields obtained are very low [61-66].

With significant amounts of bis-PCl derivatives in our hand, we were interested in exploring the possibility of their utilisation as components of polycycles.

4.2. Cyclocondensation of 8, 9 with Bistrimethylsilylether

Reaction of **8** with bistrimethylsilylether in a 1:1 molar ratio gave the polycyclic bisphosphines **35**, **37** and **39** in moderate yield (Eqn. 14). After stirring the reactants at room temperature for four days the reaction was complete, according to ^{31}P-NMR evidence. In the ^{31}P-NMR spectra of the reaction mixture, the signals of the starting material disappeared completely and new signals, due to the products, between 124-133 ppm could be seen. After removal of the solvent, the crude products were purified by crystallisation from dichloromethane and diethyl ether. The reaction of **9** with bistrimethylsilylether was carried out under the same condition. It seems that the spacer of the precursor compounds (**8, 9** and bistrimethylsilylether) does not significantly affect the reaction process.



(14)

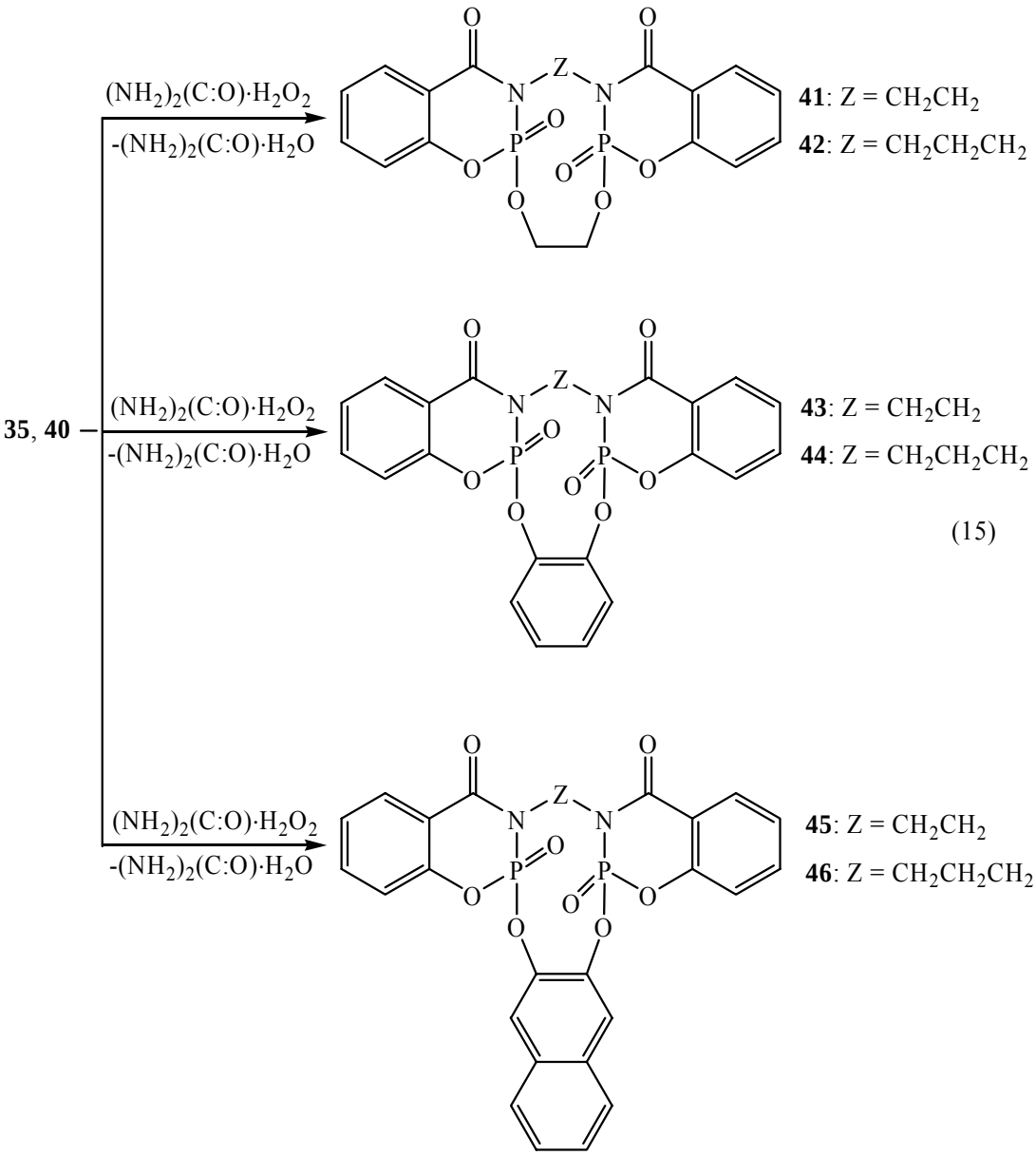
The compounds **35**, **37** and **39** display singlets in the ^{31}P-NMR spectra with a chemical shift between 124-133 ppm, in the expected region [34d]. Unlike acyclic bisphosphines [34a-34c], all cyclic compounds **35**, **37** and **39** exist as single isomer in the solution. A ^{31}P-NMR investigation of **35** in $CDCl_3$ showed that the sharp singlet remains unchanged even after one week at room temperature. However, the compounds **36**, **38** and **40** show two signals in the ^{31}P-NMR spectra at room temperature, the two phosphorus atoms in the molecules of **36**, **38** and **40** are probably different in solution and chemically not identical, there is no straightforward of explanation of this. The expected data were also obtained for the ^{1}H-NMR spectra (see Experimental Section). Compounds **35-40** are only poorly soluble in chloroform at room temperature, and good quality ^{13}C-NMR spectra could not be obtained, even after overnight pulsing.

Likewise, as it has been previously observed [34d], the ring size does play a significant role in determining the physical and chemical properties of the polycyclic molecules. **35**, **37** and **39**, involving a ten-membered ring, are considerably less sensitive to moisture. **35** can even be briefly handled in moist air without significant decomposition. In contrast to **35**, **37,** and **39**, compounds **38** and **40** are very sensitive against moisture.

4.3. Oxidation of 35-40 with $(H_2N)_2(C{:}O)\cdot H_2O_2$

It was of interest to oxidise the polycycles **35-40** since cyclic phosphoryl compounds often offer unusual chemical and physical properties, compared to their open-chain analogues. When compounds **35-40** were allowed to react with $(H_2N)_2(C{:}O)\cdot H_2O_2$, **41-46** were obtained in high yield (Eqn.15). A stepwise process with one phosphorus atom being oxidised in the first step, followed by the oxidation of the second phosphorus atom was not observed, according to ^{31}P-NMR studies. Compounds **41-46** exist as single conformers in solution at room temperature, according to NMR (^{1}H, ^{13}C and ^{31}P) investigations. It must be noted that the parent polycyclic bisphosphines **36**, **38** and **40** show two signals in chloroform solution at room temperature. After the oxidation only one signal could be seen between -1.56 to 5.70 ppm. Interestingly, the oxidised compounds were considerably more soluble in dichloromethane and chloroform, compared to their parent δ^3-bisphosphines. It is assumed that the polycyclic ring enlarged through the insertion of two oxygen atoms confers higher flexibility on the molecules.

In contrast to **35-40**, good quality ^{13}C-NMR spectra for compounds **41-46** could be recorded in chloroform. The $\delta(^{13}C)$ values of *C*:O in **41-46** lie around 162 ppm, and doublets with $^{2}J(PC)$ values of about 7.0 Hz were recorded (see Experimental Section). The oxidised compounds, **41-46** are very stable under normal conditions. In the case of **44** and **46**, molecular ions as base peak of 100% intensity in the EI-mass spectra were detected, which again indicated the high stability of the heterocyclic ring. Further fragments are presented in the Experimental Section.



(15)

4.4. X-ray structure analysis of Compound 45

Single crystals of **45** suitable for X-ray diffraction analysis were grown from $CDCl_3$/ diethyl ether solution at room temperature. The molecules **45** are potentially diastereomeric; the configuration at the chiral phosphorus atoms is, however solely SS/RR (Fig 9), corresponding to the formal twofold symmetry of the molecule. There are appreciable differences in conformation between two halves of the molecule, especially in the region P-O4-C9 (e.g. O3-P-O4-C9 –86, -123° or P-O4-C9-C10 77, 116°). A least-squares fit of both halves gives a mean deviation of 45 pm. The six-membered heterocycles do not belong to one of the standard conformations; P (P') lie 45.9 (58.6) pm outside the plane determined by the other five ring atoms; mean deviation: 1.9 (5.7) pm. The nitrogen atoms are slightly pyramidalized,

with deviations of 9.1 (N) or 1.5 pm (N') from the planes of their α-substituents. The two six-membered rings C2-C7 and C2'-C7' subtend an interplanar angle of 79.3°. The torsion angle along the bridging C_2H_4 unit is -99.1°. Intermolecular hydrogen bonds of the type C-H...O are listed in Table 1.

Tabele 1. Hydrogen bonds lengths [pm] and angles [°] for compound 45.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4')-H(4')...O(1')#1	95	239	317.9(3)	140.7
C(5)-H(5)...O(2')#2	95	254	342.4(3)	155.2
C(6')-H(6')...O(1)#3	95	260	354.3(3)	172.7
C(6)-H(6)...O(2)#4	95	248	335.2(3)	152.3

Symmetry operations for the equivalent atoms:
#1: x+1,y,z #2: x-1,-y+3/2,z+1/2 #3: -x+1,y-1/2,-z+1/2
#4: x,-y+3/2,z+1/2

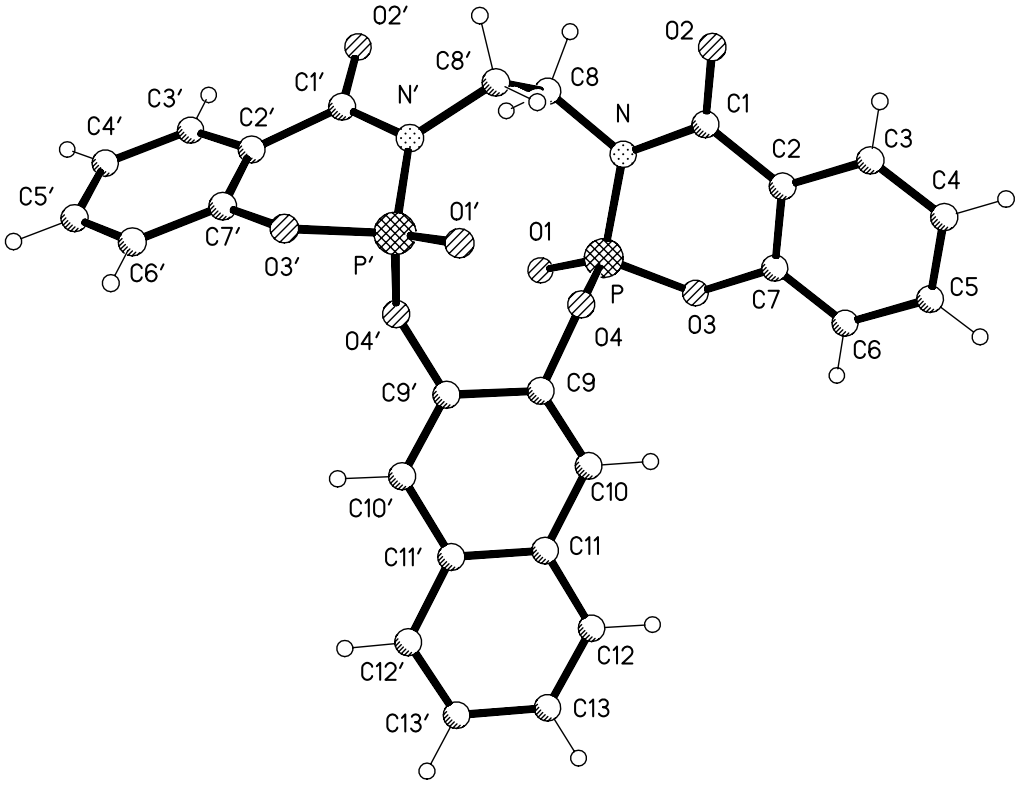
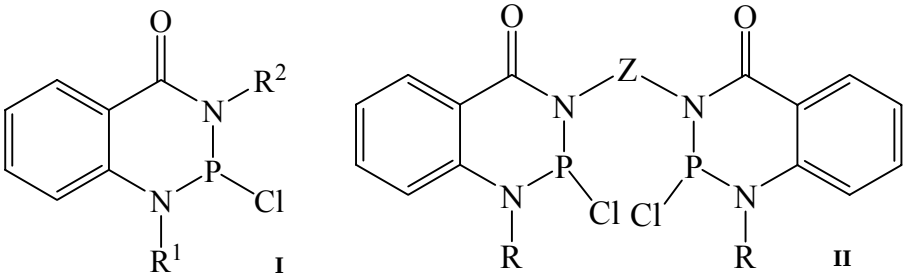


Fig.9: The formula unit of compound **45** in the crystal.. Radii are arbitrary. Selected bond lengths/pm and angles/°: P-N: 165.84(16), P'-N': 167.45(17), P-O1: 145.09(16), P'- O1': 144.68(15), P-O3: 157.73(16), P'-O3': 158.52(15), P-O4: 158.72(15), P'-O4': 158.51(14); N-P-O4: 101.29(8), N-P-O1: 116.47(9), O3'-P'-O4': 101.12(8), O1'-P'-O4': 116.99(9).

5. Phosphorus-containing polycyclic Systems II

5.1. Introduction

N-substituted 2-chloro-1,3,2-benzodiazaphosphorinanones I (Fig. 10) have been known for several decades and their derivatives have been well investigated since [61-66]. Compounds of type II (Fig. 10) containing an aliphatic $(CH_2)_n$ grouping linking two benzodiazaphosphorinanone units of type I via nitrogen have also been reported.

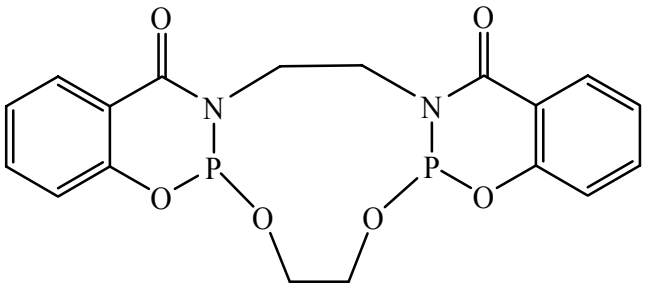


R, R^1 , R^2 = alkyl, aryl substituents

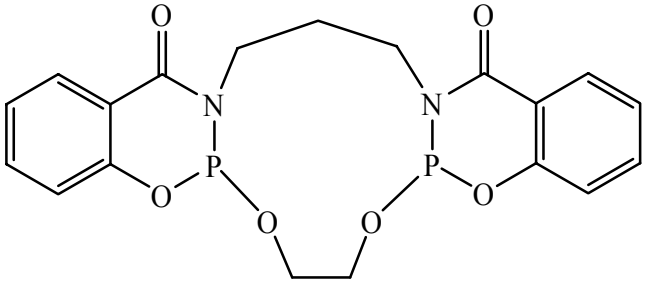
Z = CH_2CH_2, $CH_2CH_2CH_2$

Fig.10.

We have studied the synthesis of the symmetrical phosphorus-containing ring systems, involving 10- and 11-membered rings as a central feature, by the [1+1]



10-membered cycle

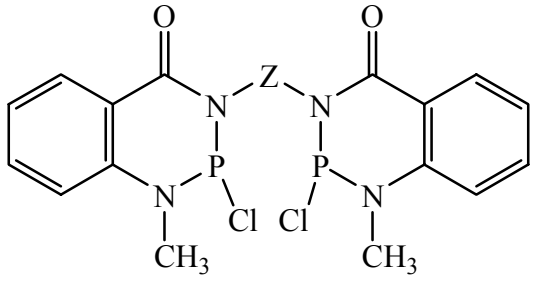


11-membered cycle

cyclocondensation of bis-(2-chloro-1,3,2-benzdiazaphosphorinanones) and bis-(2-chloro-1,3,2-benzoxazaphosphorinanones) with 1,2-bis(trimethylsilyloxy)ethane [34d]. Hereby,

spacers of different length and nature have been introduced linking two phosphorus-containing heterocycles (6-membered) to form a larger ring system (10- or 11-membered). It was found that the ring size of the central ring-system influences the chemical and physical properties of the compounds significantly. Molecule with 10 atoms in the central ring-system is considerably more stable towards moisture, compared to its chemically closest analogue with only one more atom in the ring system. Further attempts were made, introducing larger and/or bulkier spacers to link the two six-membered benzdiazaphosphorinanone units, in order to study the influence of the different spacers on the properties of large ring systems. Mixed-donor large-ring systems would be especially interesting in view of the possibility of selective chelation of different metals via P-atoms (soft donors) for transition metals, and N-atoms (hard donors) for main group metals. As part of the present investigation, the corresponding phosphine oxides and sulfides were also synthesized.

Compounds of type **6** and **7** are useful synthetic reagents for the preparation of bidentate ligands [34b, 34c], which are widely used in coordination chemistry [cross-ref]. With two active P-Cl groups in one molecule, these bis-PCl derivatives may also be used in the synthesis of phosphorus-containing polycycles [34d]. Since compounds of type **6** and **7** possess two active P-Cl groups, it is of interest to investigate the possibility of the synthesis of phosphorus-containing polycycles by the reaction of bis-PCl derivatives with diols or diamines. In the polycyclic systems, ring size is critical with regard to property and stability [39, 40]. It is also of interest to investigate the influence of the ring size on the chemical and physical properties of the polycyclic systems.



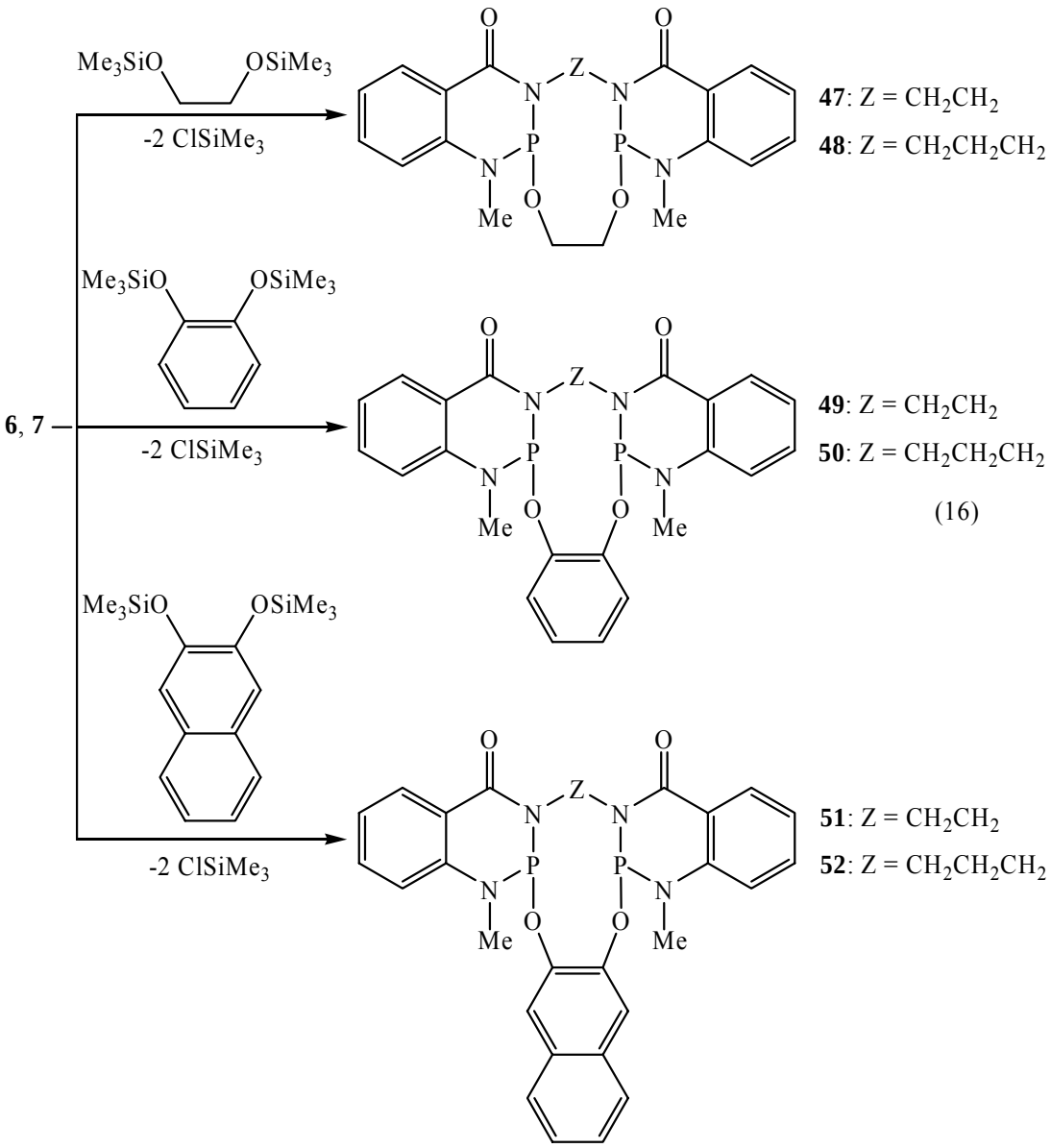
6: Z = CH_2CH_2
7: Z = $CH_2CH_2CH_2$

5.2. Cyclocondensation of 6 and 7 with 1,2-bis(trimethylsilyloxy)ethane

Procedures as described previously (see section **4.2.** on page 36 and experimental part on page 72) were employed to prepare the new large-ring systems **47-52** (Eqn. 16). A typical

[1+1] cyclocondensation of the bis-PCl derivative **6** with 1,2-bis(trimethylsilyloxy)ethane required four days stirring at room temperature. The course of the reaction was monitored by ^{31}P-NMR spectroscopy. After the reaction was complete, the signal of the starting material **6** had disappeared completely and one main peak at *ca.* 114.0 ppm was seen in the ^{31}P-NMR spectrum, representing the product **47**. The product could easily be obtained by crystallization from dichloromethane and diethyl ether after removal of the solvent, dichloromethane. The average yield of the reaction was around 60% (see Experimental Part). The high dilution method, which is usually used in the preparation of large-ring systems, did not improve the yield significantly. The reactions of **7** with the corresponding bis(trimethylsilyl)ether were carried out under the same conditions, and the products were purified in the same manner. According to ^{31}P-NMR studies the spacers in the bis-PCl derivatives **6** and **7** (the $(CH_2)_n$ groups) and in the bis(trimethylsilyl) ethers (the -OC_6H_4O- and –$OC_{10}H_6O$-groupings) do not significantly affect the course of reaction .

A temperature increase did not shorten the reaction time. In every case, more impurities and a decrease in the yield were observed.



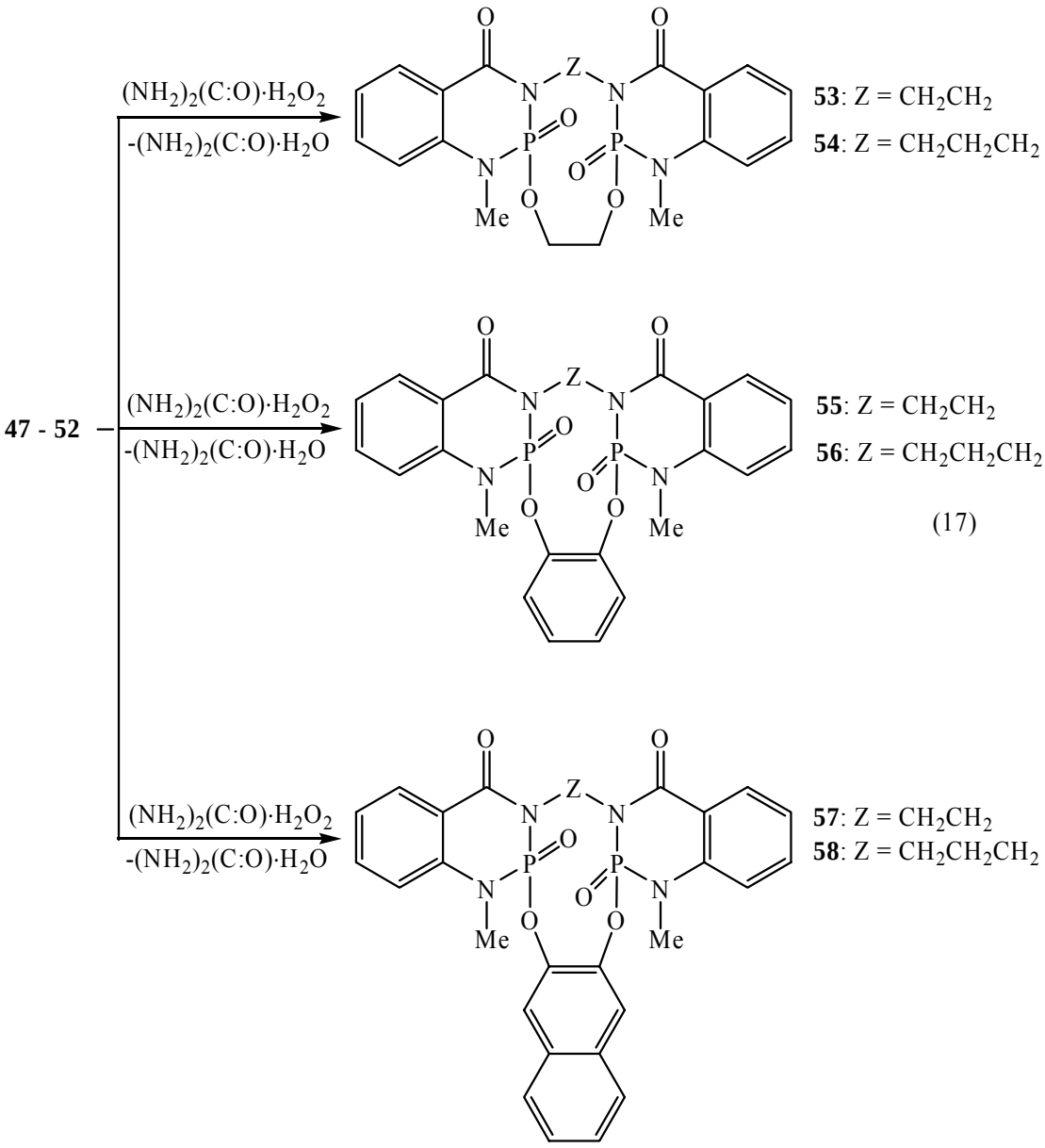
(16)

All the isolated compounds, **47-52** display one sharp singlet in their ^{31}P-NMR spectra, recorded in common solvents at room temperature, which suggests that the phosphorus atoms in the molecules are chemically equivalent. It was found that solutions of simple alkylene diphosphorus(III) compounds, bearing two benzdiazaphosphorinanone groups show a rotation process at room temperature which could cause the initial signal in the ^{31}P-NMR spectrum to be split into two signals representing two conformers in solution. This phenomenon did not occur in the case of the large-ring systems of **47-52**. A ^{31}P-NMR investigation of **47** showed that the signal at 117.5 ppm remained unchanged, even after heating the solution of sample to the reflux temperature of $CDCl_3$. It is assumed that the combination of the two small 6-membered rings by the two bridging units reduces the flexibility of the molecules, and hence confers high stability. The expected data were also

obtained for the ^{1}H and ^{13}C-NMR spectra (see Experimental Section). In the ^{1}H-NMR spectra of **47-52**, the aromatic hydrogen atoms display several multiplets in the region 6.60-8.40 ppm. The resonances of the PNCH_2 groups in the bridging units lie at 3.35-4.80 ppm as two multiplets; due to the complexities of the P-H and H-H coupling no clear coupling constant could be resolved. The only characteristic signal for all the large ring systems **47-52** is the clear sharp doublet due to the PNCH_3 protons between 3.14- 3.55 ppm. In all cases the values of $^{3}J(PH)$ lie in the region, 11.0-14.0 Hz.

5.3. Oxidation of 47-52 with $(H_2N)_2(C{:}O)\cdot H_2O_2$ and with elemental Sulfur

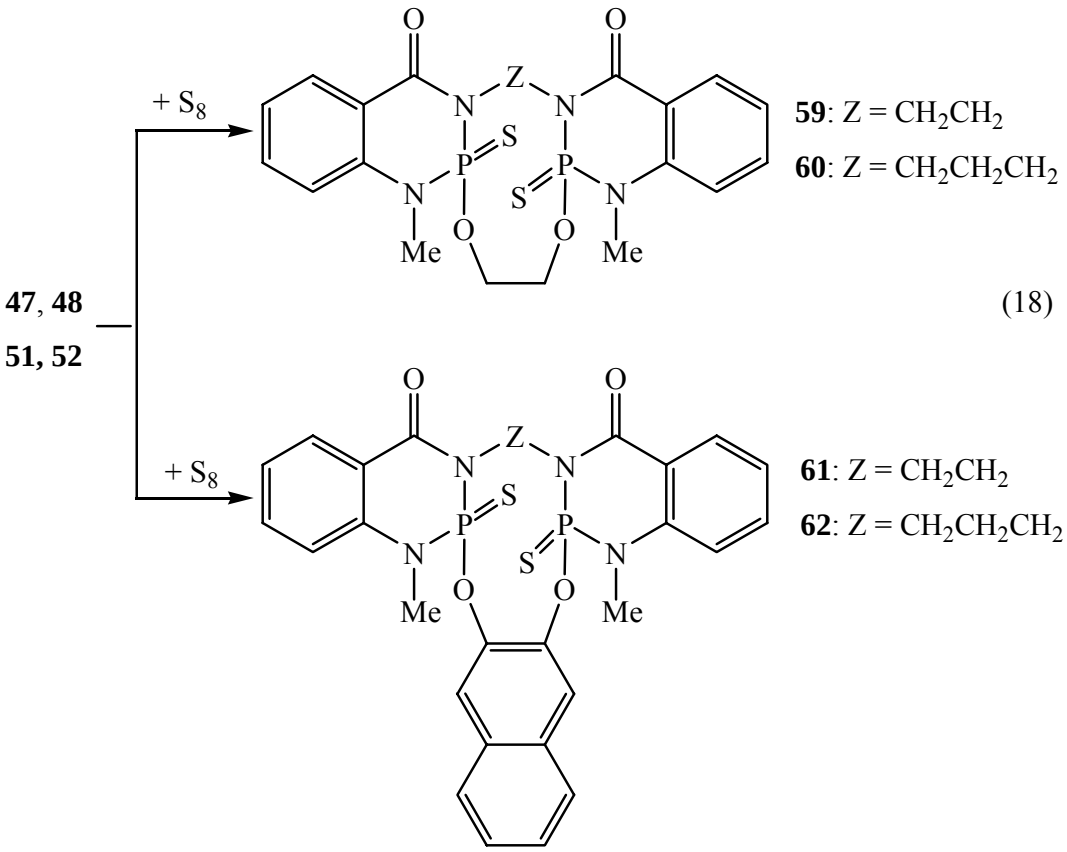
The large-ring systems **47-52** show notable stability towards common oxidizing agents such as H_2O_2 and sulfur. The reactions of compounds **47-52** with $(H_2N)_2(C{:}O)\cdot H_2O_2$ required 24 h stirring at room temperature to form compounds **53-58** (Eqn. 17). By comparison, simple alkylenediphosphorinanones of similar structure react with $(H_2N)_2(C{:}O)\cdot H_2O_2$ almost spontaneously [33, 34].



(17)

The reactions of **47** and **48** with elemental sulfur in refluxing toluene gave the corresponding sulfides **59** and **60** (Eqn.18). Similarly, the reactions of **51** and **52** gave the sulfides **61** and **62**. In each case refluxing is necessary and no reaction took place in dichloromethane at room temperature. All the compounds **59-62** exist as single conformers in the respective solvent at room temperature, as indicated by the sharp ^{31}P-NMR signals ($\delta(^{31}P)$ between 66.62 and 73.78 ppm). In the ^{1}H- and ^{13}C-NMR spectra **59-62** display similar patterns as their parent compounds **47** and **48** and **59** and **60**. The value of $^{3}J(PH)$ for PNC*H*$_3$ lies between 7.79 and 8.84 Hz, much smaller than in the parent bis(phosphorus(III)) compounds, but in line with their acyclic analogues [33, 34]. The $\delta(^{13}C)$ values for the C(:O) carbon atom in **47** and **48** and **59** and **60** lie at about 163 ppm (doublets with $^{2}J(PC)$ ca. 4.25 Hz). The compounds are all very stable under normal conditions. In the EI-mass spectra of all the compounds the

molecular ions were detected as base peaks, which again indicated the high stability of the heterocyclic rings. Further fragments are presented in the Experimental Section.



(18)

5.4. Crystal Structure investigation of Compounds 54 and 60

Compound **54** crystallizes as a dichloromethane solvate, compound **60** without solvent; thus they are not strictly isostructural, although closely similar in their structures. In the following discussion, values for **60** are enclosed in square brackets.

The molecules of **54** are diastereomeric; the conformation at the chiral phosphorus atoms is SS/RR. The six-membered heterorings show a half-boat conformation, in which the phosphorus atoms lie 47.6 [40.9] (P1) or 33.2 [50.8] pm (P1') outside the mean plane of the other five atoms (mean deviation 2.1, 2.2 [2.0, 5.1] pm, respectively). The nitrogen atoms are slightly pyramidalised, with deviations of 5.6 (N2') to 13.6 pm (N1)[6.4 (N2') to 22.1 pm (N1')] from the planes of their substituents. The two benzodiazaphosphorinanonerings subtend an interplanar angle (between the planes as defined above) of 80.4° [63.5°] and are connected via bridges $(CH_2)_3$ and $O(CH_2)_2O$ to form an eleven-membered ring. The bridge

conformations are defined by torsion angles of 68.4° [±70.0°] around C11±C11', 61.5° [±54.4°] around C9±C10 and ±168.5° [178.0°] round C10±C9'. A least-squares fit of both eleven- membered rings gave an r. m. s. deviation of 17 pm.

The solvent molecule of **54** is involved in a hydrogen bond C99-H99A···O1 with H···O 229 pm, C-H···O 170°. In **60** there is a hydrogen bond C11-H11B···O1 (x±1, y, z) with H···O 239 pm, C-H···O 162°. There are no other H···O contacts < 250 pm.

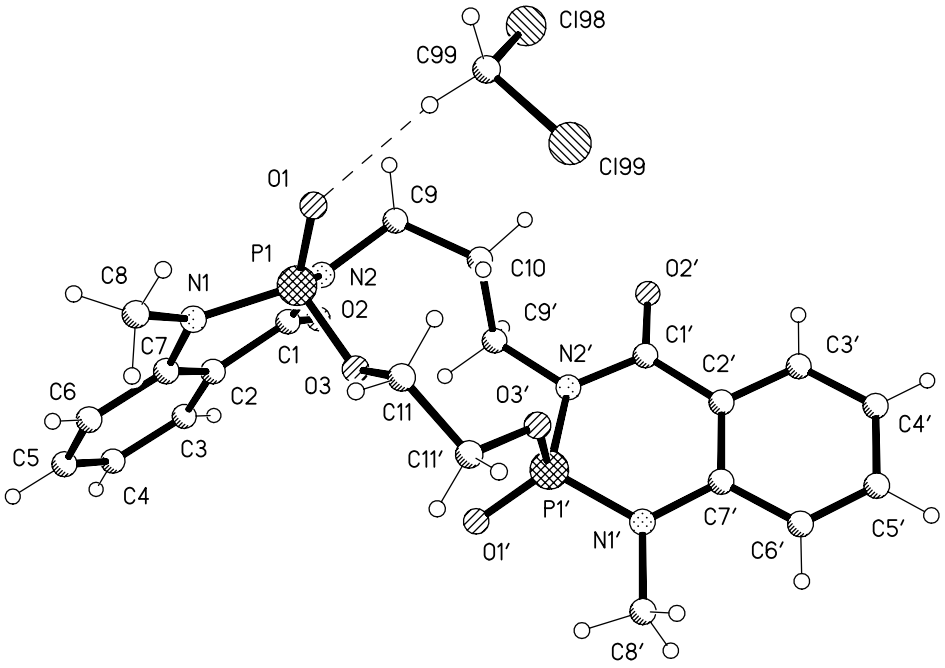


Fig. 11 The formula unit of compound **54** in the crystal. Radii are arbitrary. Selected bond lengths/pm and angles/°: P(1)-O(1) 146.09(19), P(1)-O(3) 158.93(18), P(1)-N(1) 164.5(2), P(1)-N(2) 166.9(2), P(1')-O(1') 146.08(18), P(1')-O(3') 159.12(18), P(1')-N(1') 165.0(2), P(1')-N(2') 166.9(2), O(1)-P(1)-O(3) 112.88(11), O(1)-P(1)-N(1) 115.38(12), O(3)-P(1)-N(1) 106.74(11), O(1)-P(1)-N(2) 114.71(11), O(3)-P(1)-N(2) 102.96(10), N(1)-P(1)-N(2) 102.92(11), O(1')-P(1')-O(3') 113.03(10), O(1')-P(1')-N(1') 114.52(11), O(3')-P(1')-N(1') 107.77(10), O(1')-P(1')-N(2') 114.94(10), O(3')-P(1')-N(2') 102.53(10), N(1')-P(1')- N(2') 102.86(10).

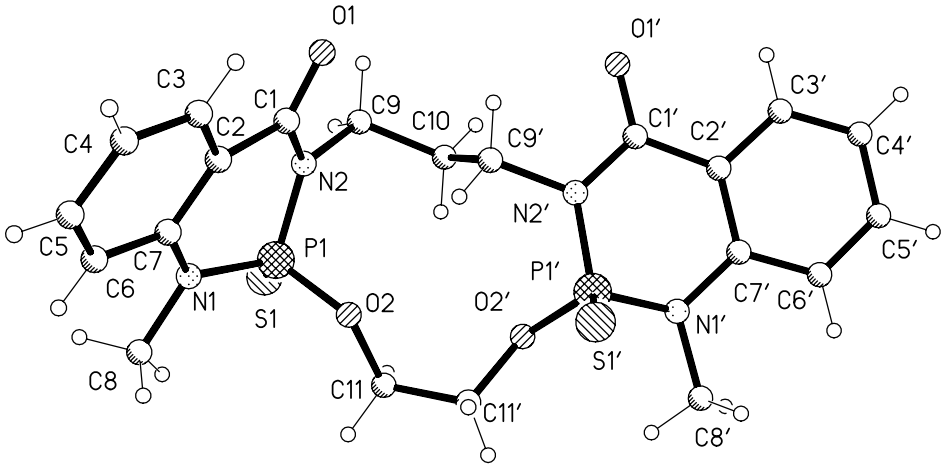


Fig. 12 The formula unit of compound **60** in the crystal. Radii are arbitrary. Selected bond lengths/pm and angles/°: P(1)-O(2) 160.07(18), P(1)-N(1) 165.84(19), P(1)-N(2) 167.32(18), P(1)-S(1) 191.75(17), P(1')-O(2') 158.41(19), P(1')-N(1') 165.90(18), P(1')-N(2') 167.4(2), P(1')-S(1') 191.80(13), O(2)-P(1)-N(1) 106.62(9), O(2)-P(1)-N(2) 102.16(11), N(1)-P(1)-N(2) 102.94(8), O(2)-P(1)-S(1) 113.42(7), N(1)-P(1)-S(1) 115.38(7), N(2)-P(1)-S(1) 114.91(10), O(2')-P(1')-N(1') 103.60(8), O(2')-P(1')-N(2') 101.60(9), N(1')-P(1')-N(2') 101.56(8), O(2')-P(1')-S(1') 114.37(8), N(1')-P(1')-S(1') 116.73(7), N(2')-P(1')-S(1') 116.83(9).

5.5. Single Crystal X-ray investigation of Compounds of 51, 56, 57, 58 and 61

Though all the molecules discussed are potentially diastereomeric, the configuration at the chiral phosphorus atoms is solely SS/RR, as would be expected from the formal twofold symmetry of the molecules. The two halves of the central ten-membered macrocycles are more similar than those of the eleven-membered ones. For this reason the compounds with the ten-membered macrocycle (**51**, **57** and **61**, Figs. 2, 4 and 6) and those with the eleven-membered ring (**56** and **58**, Figs. 3 and 5) are discussed separately.

The approximate twofold symmetry in **51** is reflected, e. g. in the similar torsion angles N1-P-O2-C10 (104.7°) and N1'-P'-O2'-C10' (108.1°); the difference in **61** is somewhat larger (-101.1 and -116.7°). In compound **57**, with exact crystallographic symmetry, there is one independent value (N1-P-O3-C10) of -104.8°. For P-O2-C10-C11 and P'-O2'-C10'-C11', the difference in compound **51** (-105.6 and -96.5) is larger than in **61** (91.1 and 84.5°); the value for **57** is 90.5°. The torsion angle at the ethylene backbone is 117.0° (**51**), -141.2° (**57**) or -143.3° (**61**).

The aromatic rings C2-C7 or C2'-C7' subtend an interplanar angle of 68.8° (**51**), 38.4° (**57**) or 32.2° (**61**). The six-membered heterocycles in each case display a conformation in which the phosphorus atom lies (by between 20.2 (**57**) and 51.6 pm (**51**)) outside the plane formed by the five other ring atoms, the mean deviations of these planes being 1.5 - 3.5 pm.

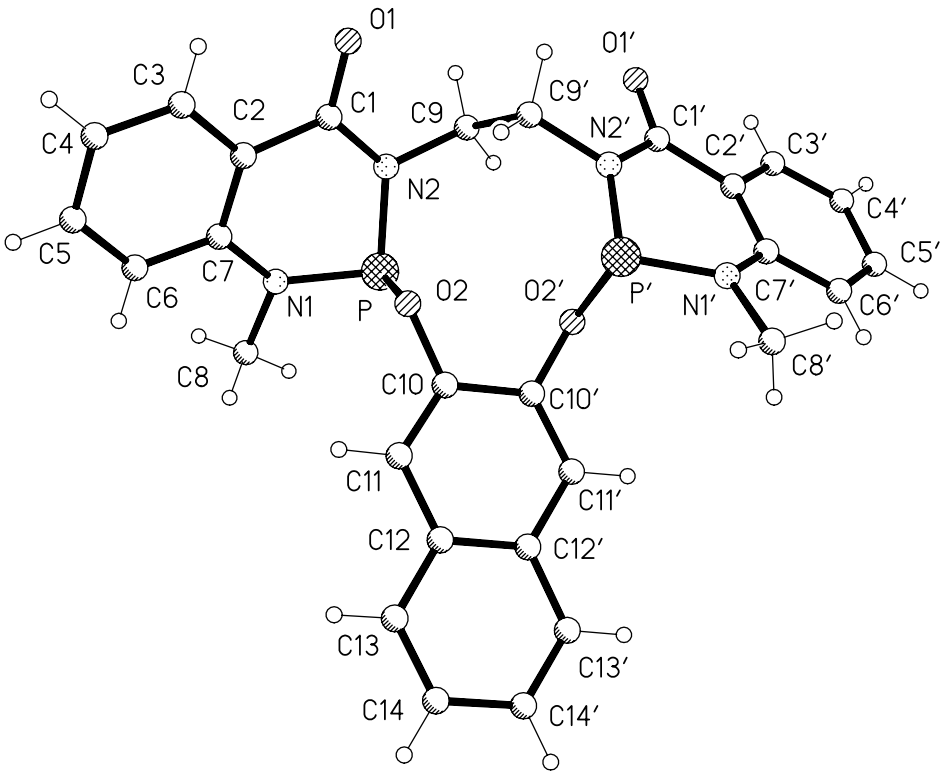


Fig. 13 The molecule of **51** in the crystal. Radii are arbitrary. Selected bond lengths/pm and angles/°: P-N1: 167.76(10), P'-N1': 167.90(10), P-O2: 168.68(9), P'-O2': 169.17(9), P-N2: 170.29(10), P'-N2': 169.98(10); N1-P-O2: 102.65(5), N1'-P'-O2': 102.42(5), N1-P-N2: 98.90(5), N1'-P'-N2': 99.36(5), O2-P-N2: 95.11(4), O2'-P'-N2': 96.93(4).

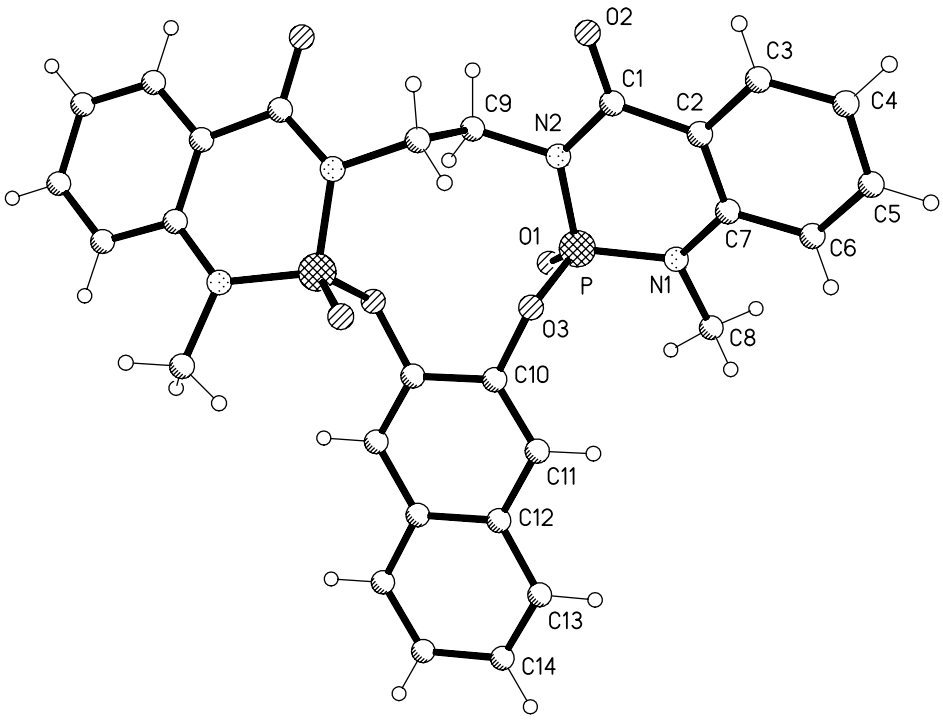


Fig. 14 The molecule of **57** in the crystal. Radii are arbitrary. Selected bond lengths/pm and angles/°: P-O1: 146.43(11), P-O3: 160.57(11), P-N1: 164.21(13), P-N2: 166.23(13); O1-P-O3: 111.46(6), O1-P-N1: 114.62(7), O3-P-N1: 108.55(6), O1-P-N2: 116.64(7), O3-P-N2: 100.70(6), N1-P-N2: 103.64(6).

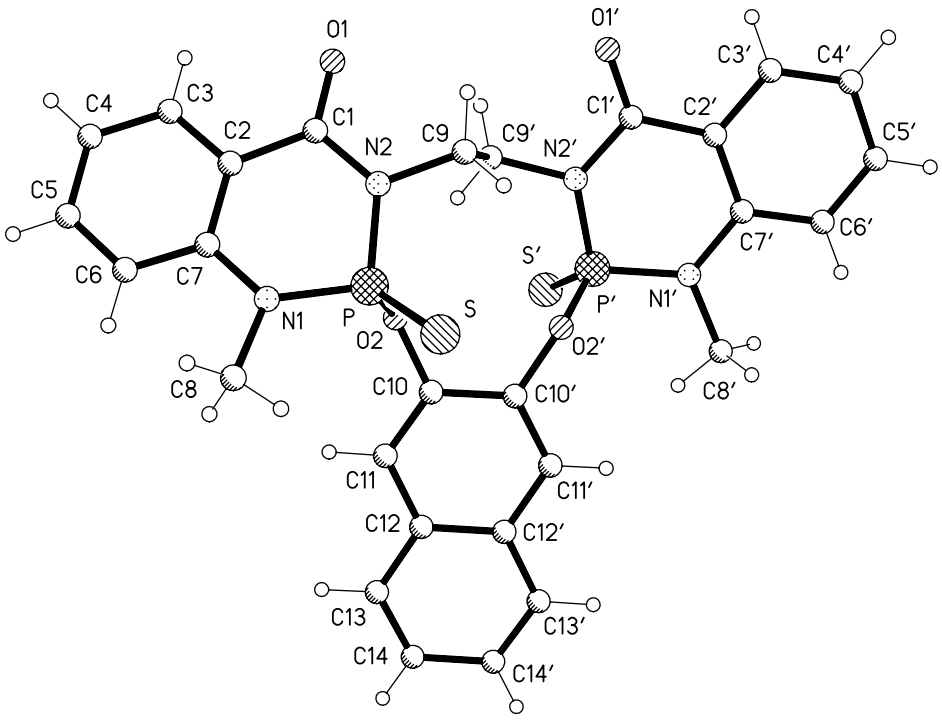


Fig. 15 The molecule of **61** in the crystal. Radii are arbitrary. Selected bond lengths/pm and angles/°: P-O2: 161.94(16), P'-O2': 160.90(16), P-N1: 164.4(2), P'-N1': 165.2(2), P-N2: 166.8(2), P'-N2': 167.7(2), P-S: 192.17(9), P'-S': 192.40(9); O2-P-N1: 108.98(10), O2'-P'-N1': 105.03(10), O2-P-N2: 98.06(9), O2'-P'-N2': 101.55(9), N1-P-N2: 102.91(10), N1'-P'-N2': 102.34(10), O2-P-S: 112.99(7), O2'-P'-S': 112.45(7), N1-P-S: 115.08(9), N1'-P'-S': 117.05(8), N2-P-S: 117.07(9), N2'-P'-S': 116.57(8).

Perhaps because of the odd number of atoms in the eleven-membered rings, the molecules of **56** and **58** depart very considerably from twofold symmetry. Nevertheless, the eleven-membered rings in **56** and **58** display very similar torsion angles (see Fig. 7). Looking along the plane of the benzo or naphtho group, in which O3, C11, C11' and O3' lie, it can be seen that in both cases C9, P and N2 lie on one side of this plane, and C10, C9', P' and N2' on the other.

The conformation of the six-membered heterocycles is noteworthy in that in both molecules the unprimed ring displays small absolute torsion angles (1.8 -11.6° (**56**) and 3.3 - 7.8° (**58**)) and the primed ring a much less planar conformation with larger torsion angles (6.3 - 44.1° (**9**) and 8.1 - 44.1° (**58**)). The phosphorus atoms lie 12.5 and –63.5 pm (**56**) and 0.8 and 64.4 pm (**58**) out of the plane of the other ring atoms.

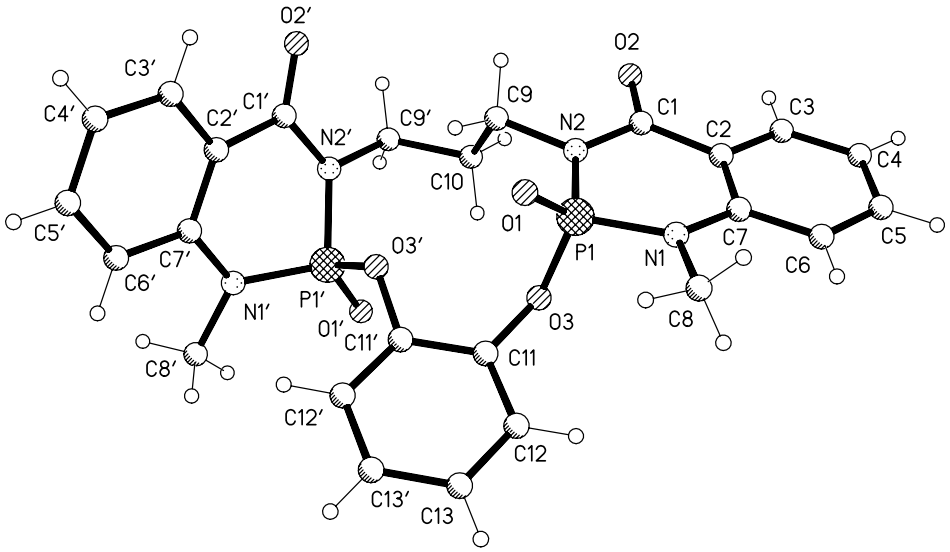


Fig. 16 The molecule of **51** in the crystal. Radii are arbitrary.Selected bond lengths/pm and angles/°: P1-O1: 146.37(14), P1'-O1': 145.97(15), P1-O3: 161.06(14), P1'-O3': 160.79(15), P1-N1: 164.55(16), P1'-N1': 164.09(17), P1-N2: 166.05(16), P1'-N2': 166.83(17); O1-P1-O3: 111.00(8), O1'-P1'-O3': 114.79(8), O1-P1-N1: 115.21(8): O1'-P1'-N1': 115.13(9), O3-P1-N1: 106.68(8), O3'-P1'-N1': 107.47(8), O1-P1-N2: 115.72(8), O1'-P1'-N2': 116.45(9), O3-P1-N2: 103.28(8), O3'-P1'-N2': 97.67(8), N1-P1-N2: 103.86(8), N1'-P1'-N2': 103.85(8).

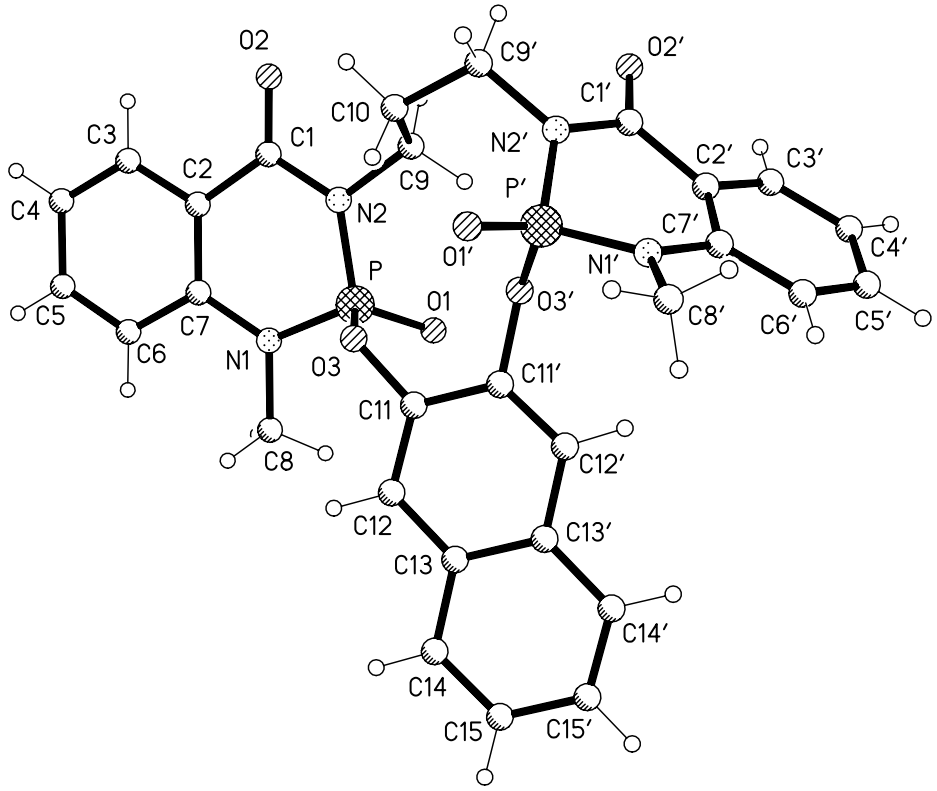


Fig. 17 The molecule of **58** in the crystal. Radii are arbitrary. Selected bond lengths/pm and angles/°: P-O1: 145.64(17), P'-O1': 145.34(17), P-O3: 161.94(16), P'-O3': 160.64(18), P-N1: 163.74(19), P'-N1': 163.55(19), P-N2: 166.1(2), P'-N2': 166.05(17); O1-P-O3: 109.42(9), O1'-P'-O3': 114.68(9), O1-P-N1: 115.97(10): O1'-P'-N1': 114.56(10), O3-P-N1: 106.08(9), O3'-P'-N1': 106.92(10), O1-P-N2: 116.35(9), O1'-P'-N2': 117.43(10), O3-P-N2: 103.81(9), O3'-P'-N2': 97.10(9), N1-P-N2: 104.08(9), N1'-P'-N2': 104.18(9).

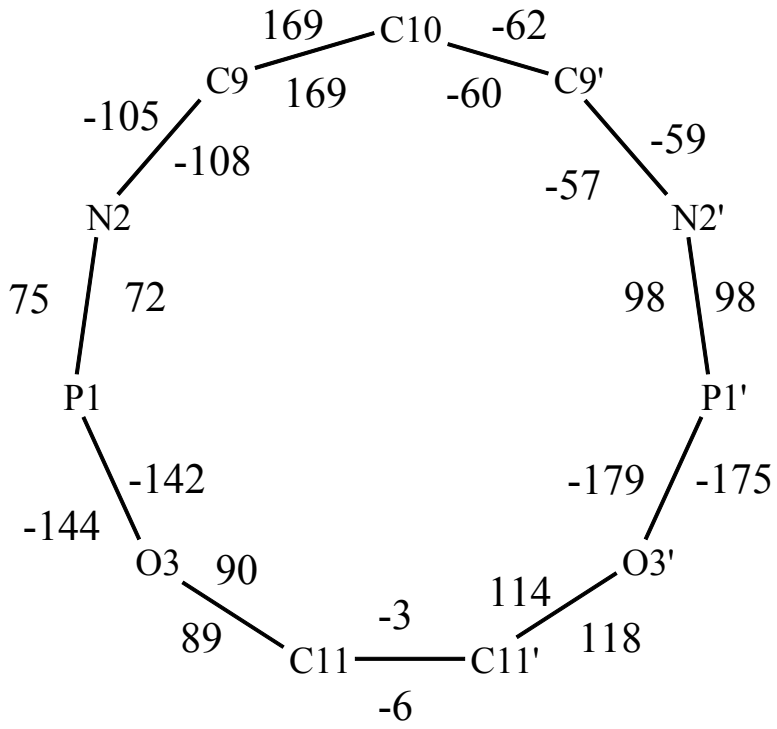


Fig. 18 Comparison between the torsion angles in the eleven-membered ring of compound **56** (outer ring) and **58** (inner ring).

All compounds display short H···O contacts that could be interpreted as hydrogen bonds (Table 1-4). Particularly short are the following: **51**, C99-H99B (ordered solvent)···O1 221 pm; **56**, C9'-H9'2···O1 243 pm; **57**, C99-H99 (ordered solvent)···O2 229 pm; **58**, C15-H15···O2' 242 pm; **61**, C99-D99 (ordered solvent)···O1' 237 pm.

Table 1. Hydrogen bonds for 51 [pm] and [°].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(8)-H(8C) ···O(1)#1	98	248	333.92(16)	146.4
C(99)-H(99B) ···O(1)#2	99	221	314.74(16)	157.0
C(4)-H(4) ···O(2)#3	95	256	337.88(16)	144.7
C(8')-H(8'3) ···O(1')#4	98	249	333.52(16)	144.1
C(14')-H(14') ···O(1')#5	95	249	343.79(15)	171.8

Symmetry transformations for the equivalent atoms:

#1 -x+1, -y, -z+1 #2 x, y+1, z #3 -x, -y, -z+1; #4 –x + 1, -y, -z #5 x-1, y+1,z

Contacts to disordered solvent are omitted.

Table 2. Hydrogen bonds for 56 [pm] and [°].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9')-H(9'2)...O(1)#2	99	243	341.2(2)	174.1
C(5')-H(5')...O(1)#1	95	259	322.7(3)	124.7
C(8)-H(8A)...O(1')#3	98	249	344.9(3)	166.5
C(8')-H(8'3)...O(2')#4	98	259	355.2(3)	167.9

Symmetry transformations for the equivalent atoms:

#1 -x+1,-y+1,-z #2 x+1,y,z #3 -x+1,-y+1,-z+1

#4 -x+2,-y+1,-z

Contacts to disordered solvent are omitted.

Table 3. Hydrogen bonds for 57 [pm] and [°].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(8)-H(8C)...O(1)#1	98	259	354.0(2)	162.9
C(11)-H(11)...O(1)#1	95	262	354.46(18)	165.4
C(99)-H(99)...O(2)#2	99	229	326.5(2)	167.7

Symmetry transformations for the equivalent atoms:

#1 x,-y,z-1/2 #2 -x+1,-y+1,-z+1

Table 4. Hydrogen bonds for 58 [pm] and [°].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(15)-H(15)...O(2')#1	95	242	316.6(3)	135.3
C(5')-H(5')...O(1)#2	95	252	317.8(3)	126.3
C(9')-H(9'2)...O(1)#3	99	245	339.3(3)	159.3
C(8)-H(8A)...O(1´)#4	98	256	343.2(3)	147.4
C(8)-H(8B)...O(1´)#5	98	258	338.1(3)	139.2

Symmetry transformations for the equivalent atoms:

#1 x-1, y-1,z; #2 –x +1, -y+2,-z-1; #3 x+1, y, z; #4 -x+1, -y+2, -z; #5 x-1, y, z.

Table 5. Hydrogen bonds for 61 [pm] and [°].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(99)-D(99)...O(1')#1	100	237	321.9(3)	142.3
C(6')-H(6')...Cl(1)#2	95	294	387.4(3)	166.1
C(5')-H(5')...Cl(2)#2	95	293	375.4(3)	146.1
C(3')-H(3')...Cl(3)#3	95	295	381.4(3)	151.8

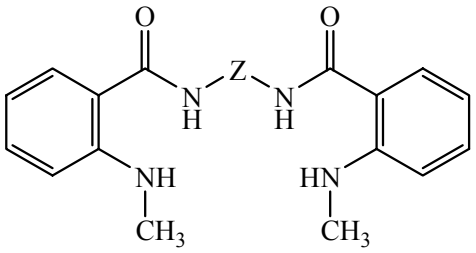
Symmetry transformations for the equivalent atoms:

#1 x,y,z+1 #2 -x,-y+1,-z+2 #3 x,-y+1/2,z-1/2

6. Conclusion and Future Outlook

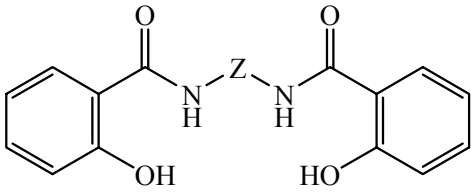
6.1. Conclusion

This thesis is concerned with the study of synthesis and reactivity of phosphorus-containing oligocyclic ring systems, including bidentate phosphorinanones and polycyclic phosphorinanones. The initial step is to establish a synthetic route for a series of chlorophosphine precursors containing different bridging units. For this purpose, a series of bisamides **1**-**5** are synthesed by introducing a alkylene bridging group to link two amide moieties, which contain either NH, NH or NH, OH groups. All these bisamides are air-stable and are characterised by ^{1}H and ^{13}C NMR spectroscopy, EI-MS spectroscopic methods, and elemental analysis. The bisamide **5** is poorly soluble in common organic solvents such as dichloromethane, chloroform, thf, toluene or diethyl ether.



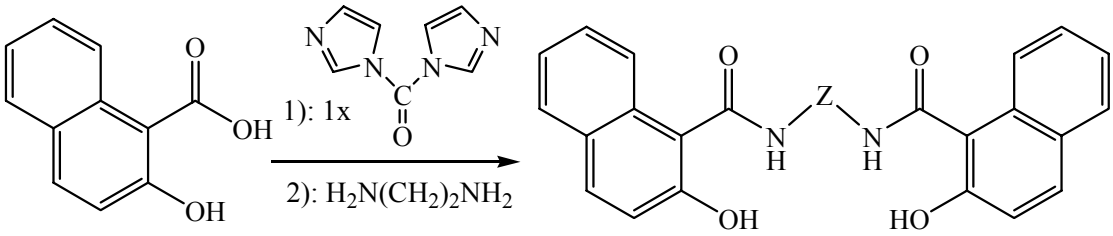
1: Z = CH_2CH_2

2: Z = $CH_2CH_2CH_2$



3: Z = CH_2CH_2

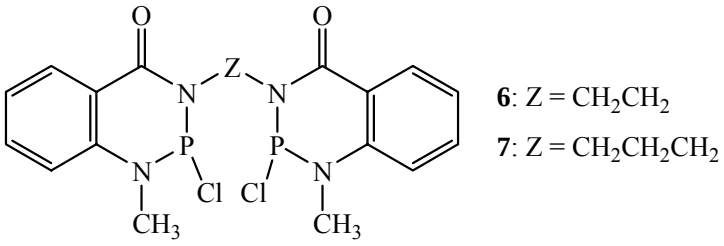
4: Z = $CH_2CH_2CH_2$



5 Z = CH_2CH_2

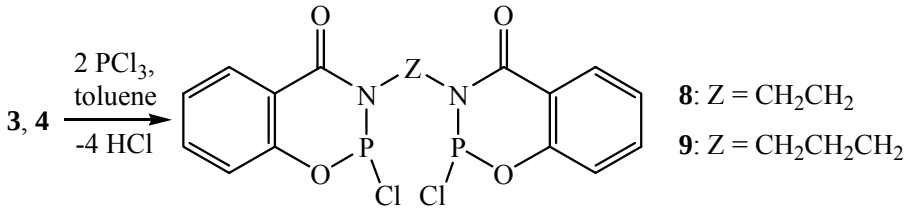
The reaction of these bisamides with phosphorus trichloride afford the desired chlorophosphine derivatives **6**-**10**. The reaction is a clear process and the resulting HCl is easily removed as a gas from the reaction mixtures (in dichloromethane or toluene) by

heating. Despite the existence of four active OH/NH groups in one molecule, the reaction of the bisamides with PCl_3 gives selectively the intramolecular condensation product in near quantitative yield. Bearing two P-Cl groups, these compounds are very reactive and decompose immediately on exposure to moisture to give rise to the corresponding P(:O)H species.



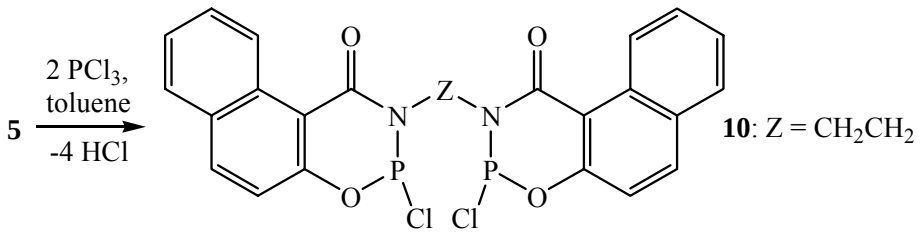
6: Z = CH_2CH_2

7: Z = $CH_2CH_2CH_2$



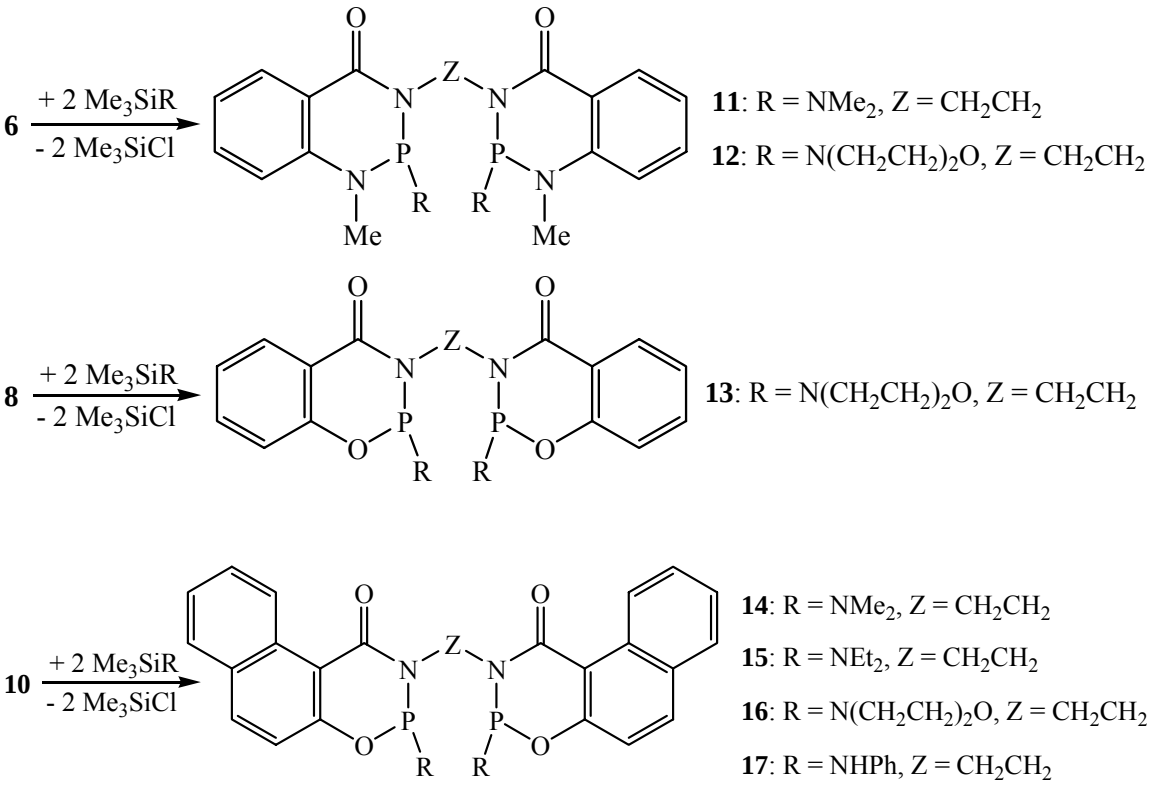
8: Z = CH_2CH_2

9: Z = $CH_2CH_2CH_2$



10: Z = CH_2CH_2

By the reaction of the bis-PCl species **6-10** with trimethylsilyl-substituted amines, a number of polycyclic bidentate ligands **10-17** are formed in high yield. The reactions involve a Si-N cleavage with formation of the P-N bond. Conformerisation reactions in solution yielding mixtures of conformers of all the compounds **10-17** are observed, and the mechanism is discussed. **10-17** are stable in an inert atmosphere, but decompose back to the bisamide on exposure to the moisture.



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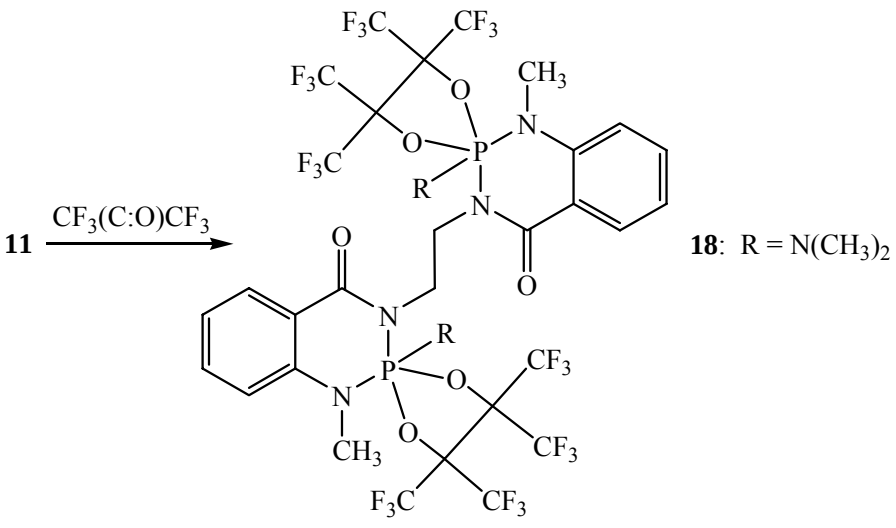
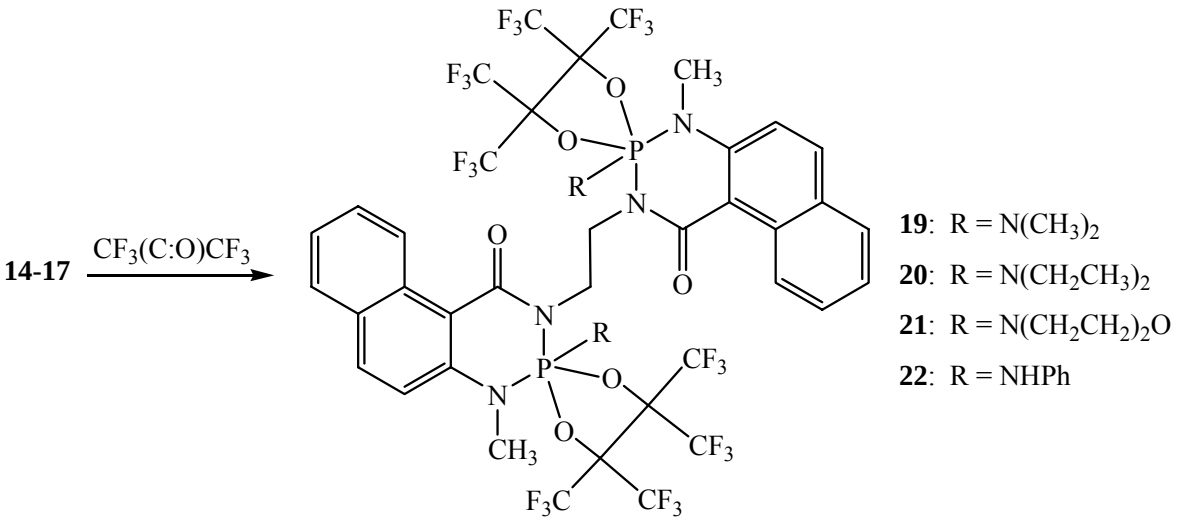
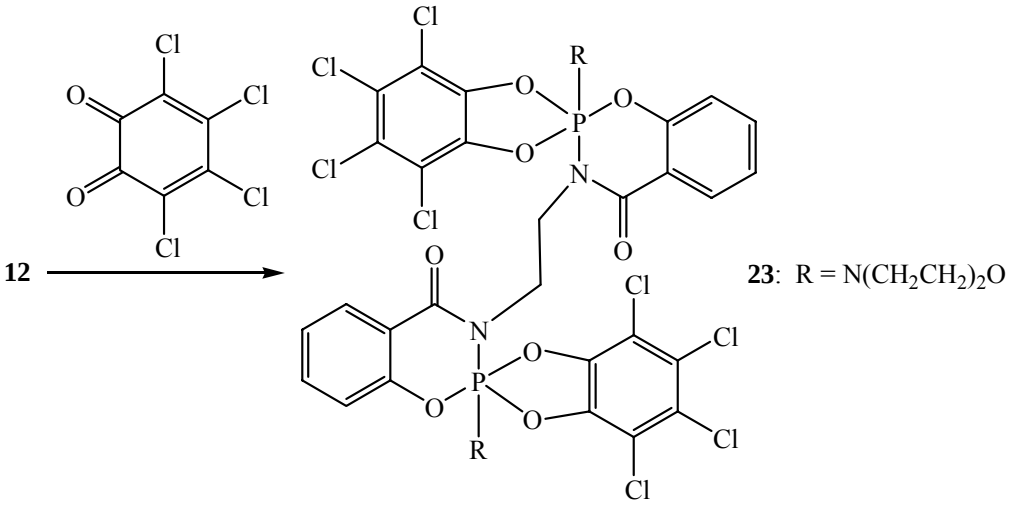
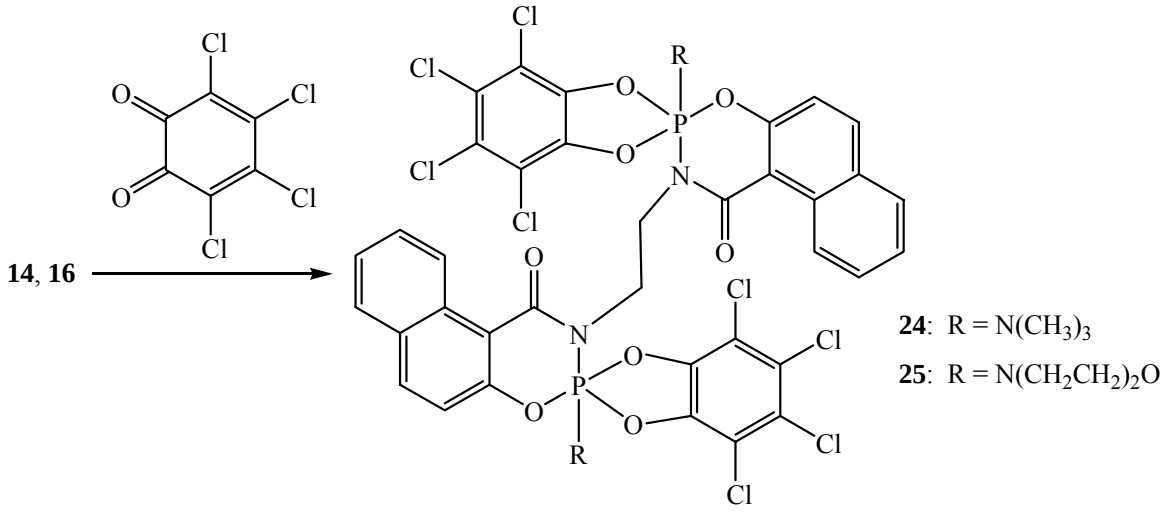
Oxidation reaction of some selected compounds by hexafluoroaceton (HFA) are investigated, and a series of five-coordinated phosphorus compounds **18-25** are isolated. In solution, most of the compounds can undergo conformerization, so that two phosphorus atoms can be observed in the ^{31}P NMR spectra. By recrystallization, single crystal one conformer of **60** can be obtained and are characterized by X-ray diffraction.



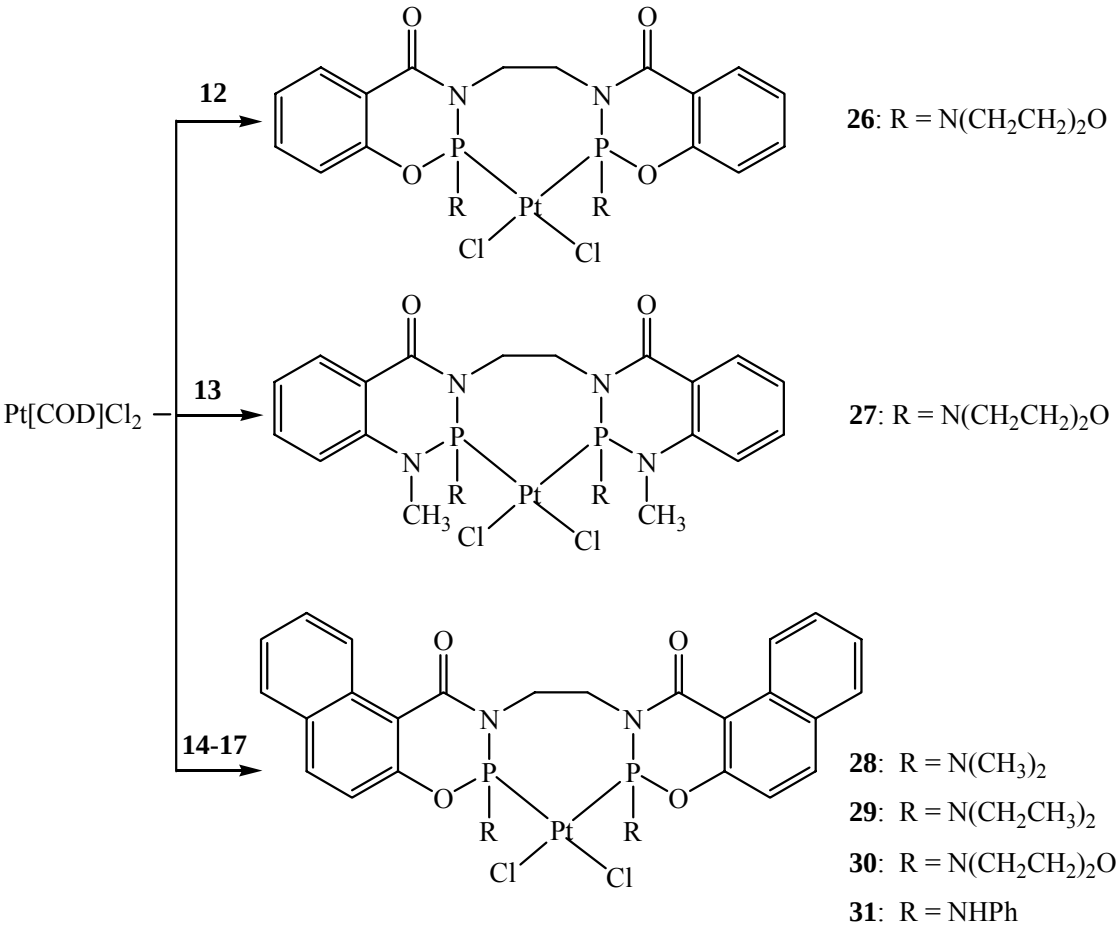


Similar reactions of some compounds with tetrachlororthobenzochinon (TOB) gave the new compounds **23-25** in high yield. Unlike **18-22**, all the bisphosphoranes **23-25** are only marginally soluble in dichloromethane or chloroform and not soluble in diethyl ether or toluene. The presence of a large number of chlorine atoms in the molecules may contribute to the existence of complex intermolecular hydrogen bonding, leading to the aggregation of the molecules, and reduce the solubility. All these compounds of **23-25** are very stable, and give rise of molecular ions as base peaks in the EI-MS spectra.

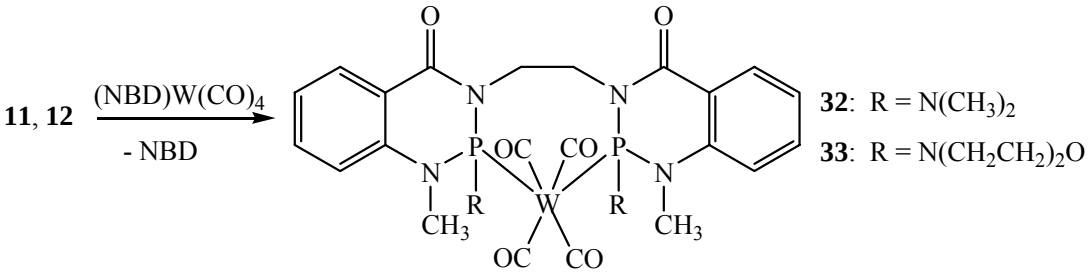




The phosphorus atoms in all the compounds **11**-**17** are linked to two potential electron donating atoms, i.e. nitrogen or oxygen. The phosphorus atoms are electron-rich. A series of transition metal complexes **26**-**34,** with Pt and W as metals, are prepared. By reaction of **12**-**17** with Pt[COD]Cl_2, a new inorganic ring is formed with two phosphorus atom chelating to the metal centre. Two of the platinum complexes **28** and **30** are analysed by single X-ray diffraction methods, and the results show that the two chlorine atoms are in *cis*-position, which is in agreement with the ^{31}P NMR observations which shows small J(P-Pt) values. Because of the complexation with platinum the two halves of the molecules are forced to the same orientation in both **28** and **30**. The Pt-P bond lengths in the two molecules show the expected shortening effect, caused by electronegative substituents at phosphorus, and the Pt-Cl bond lengths in both complexes are within the same range.

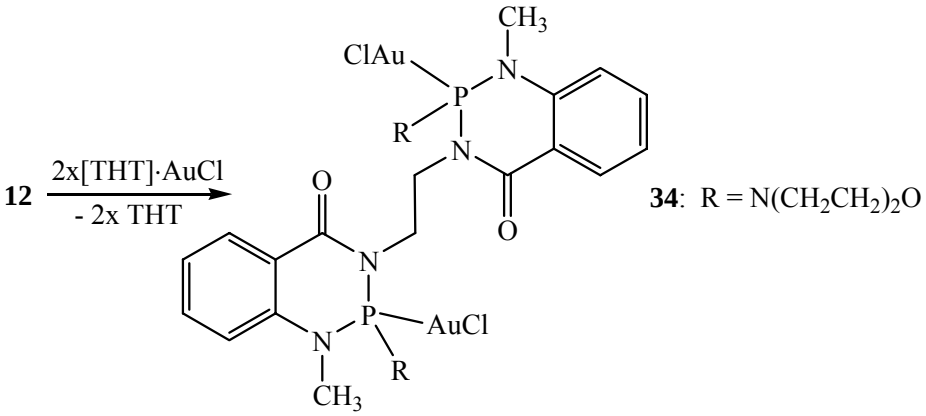


By the reaction of **11** and **12** with [NBD]W(CO)$_4$ the new complexes **32** and **33** are obtained. During the reaction, a seven-membered ring containing tungsten is formed. Similar to the free ligands, the compound **32** displays two signals at 149.3 and 147.3 ppm in the ^{31}P-NMR spectrum in $CDCl_3$ at room temperature, while compound **33** shows only one signal at 147.7 ppm. Both compounds exhibit strong molecular peaks in the MS-EI spectra.

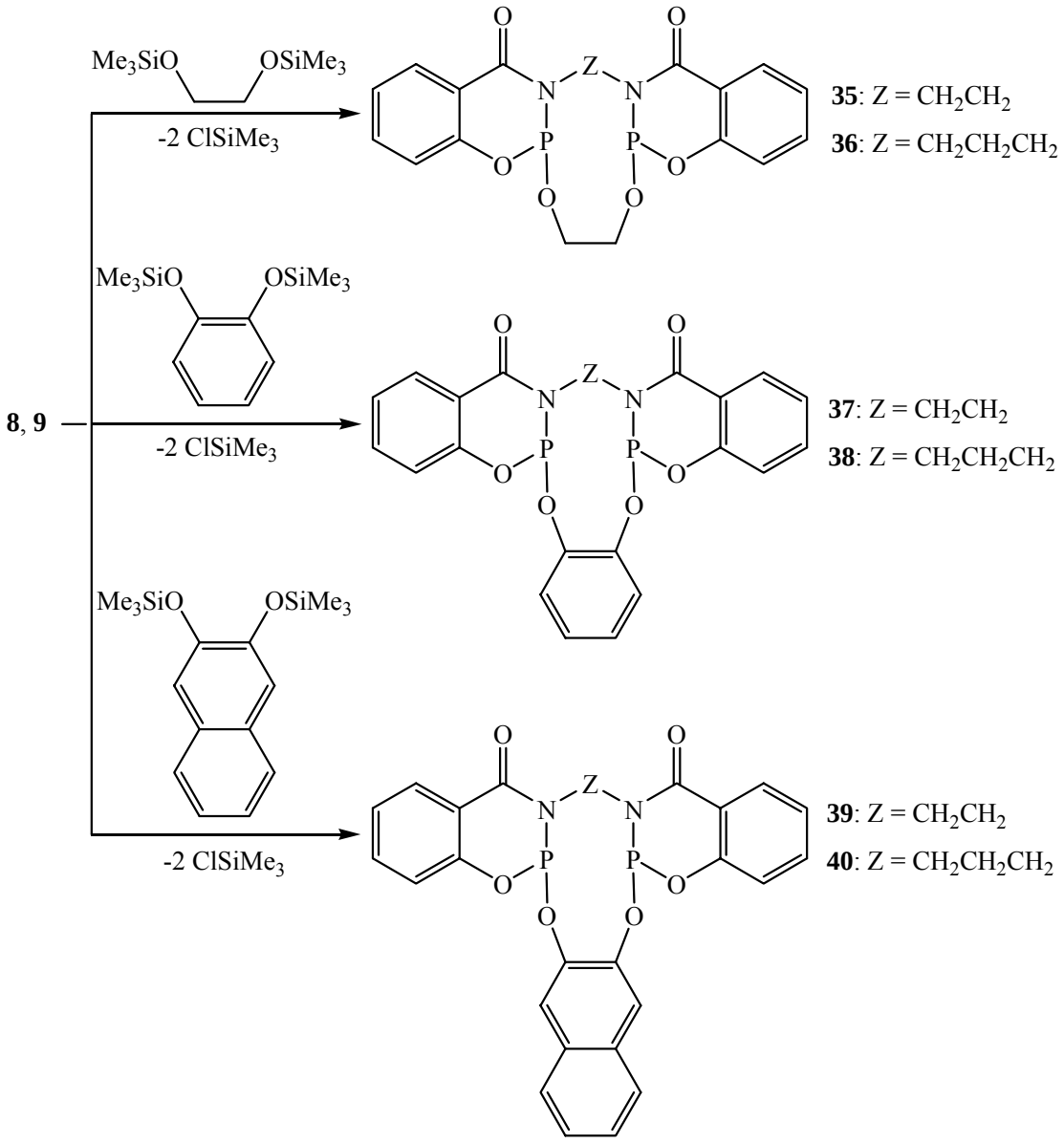


Reaction of **12** with [THT]·AuCl (THT = tetrahydrothiophen) afforded the digold complex **34**. The compound **34** displays two signals at 93.9 and 93.2 ppm in the ^{31}P-NMR spectra in

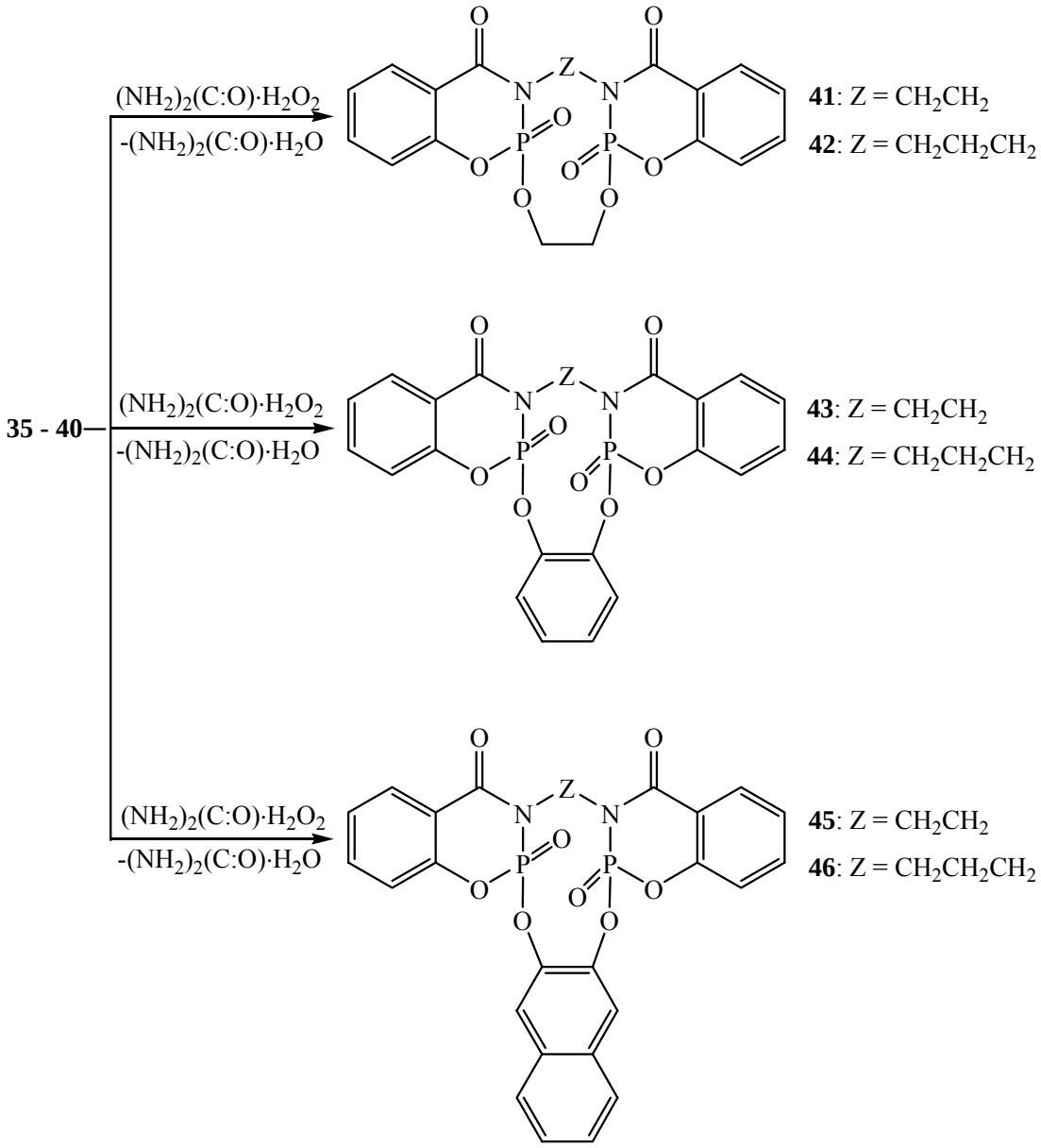
$CDCl_3$ at room temperature, indicating two conformers co-existing in the solution. **34** decomposes readily on exposure to daylight, forming a black powder.



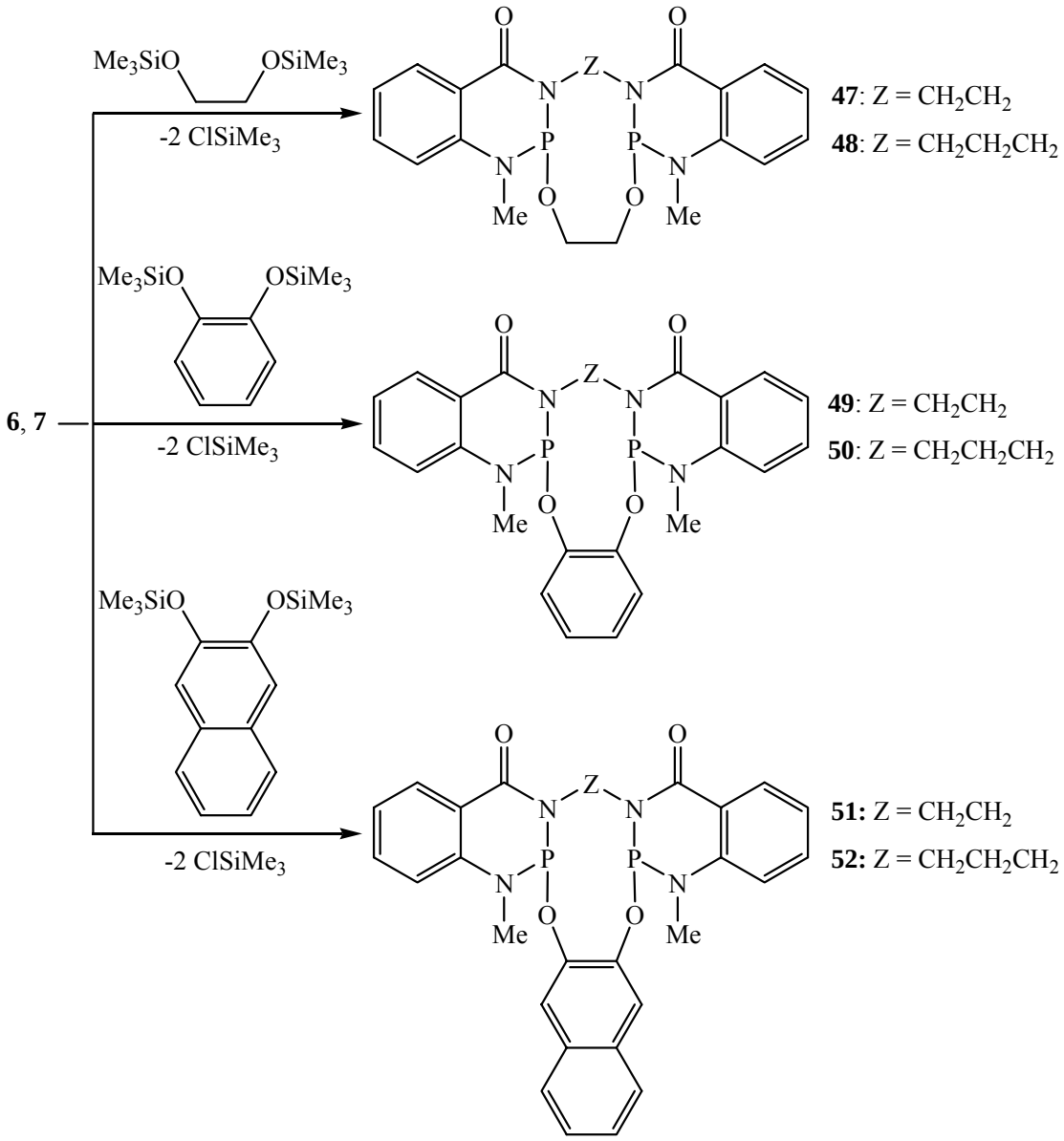
The crown ether-like phosphorus-containing polycyclic compounds **35-40** are obtained from the reaction of the bis-PCl compounds **8** and **9** with a series of bistrimethylsilylethers. The process involves condensation of two active components but interestingly, does not require the high-dilution conditions which is usually the case in synthesis of polycyclic systems. The products are all obtained in moderate to high yield and in high purity. They are more stable than the acyclic compounds and do not undergo conformerisation reactions in solution. The polycyclic compounds of differing ring-size differ significantly in their chemical reactivities, as well as in their physical properties.



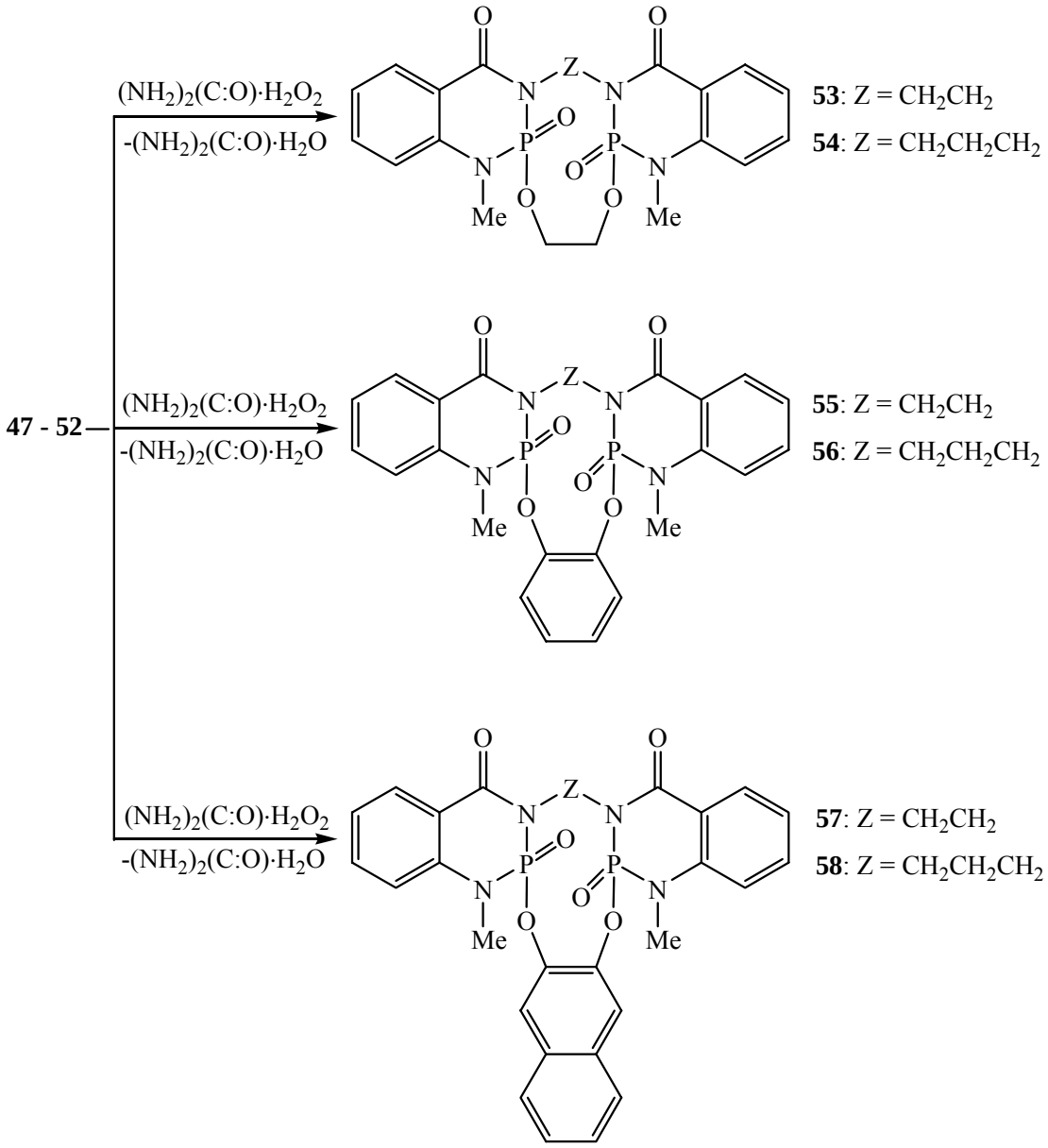
Oxidation of the polycyclic compounds **35-40** with $(NH_2)_2(C{:}O)\cdot H_2O_2$ gave the polycyclic phosphoryl compounds **41-46**. All the oxidized polycylic compounds were obtained in high yield, and no decomposition reactions were observed, indicating the high stability of the ring systems. All the new compounds displayed a single signal in the ^{31}P-NMR spectra, suggesting that only one conformer exists in solution. And no splitting information could observed in the chemical shift in the ^{31}P-NMR spectra, even was the sample left in solution for a long time. A single crystal of **45** was obtained and was analysed by X-ray diffraction, which showed several types of inter- and intramolecular hydrogen bonding.



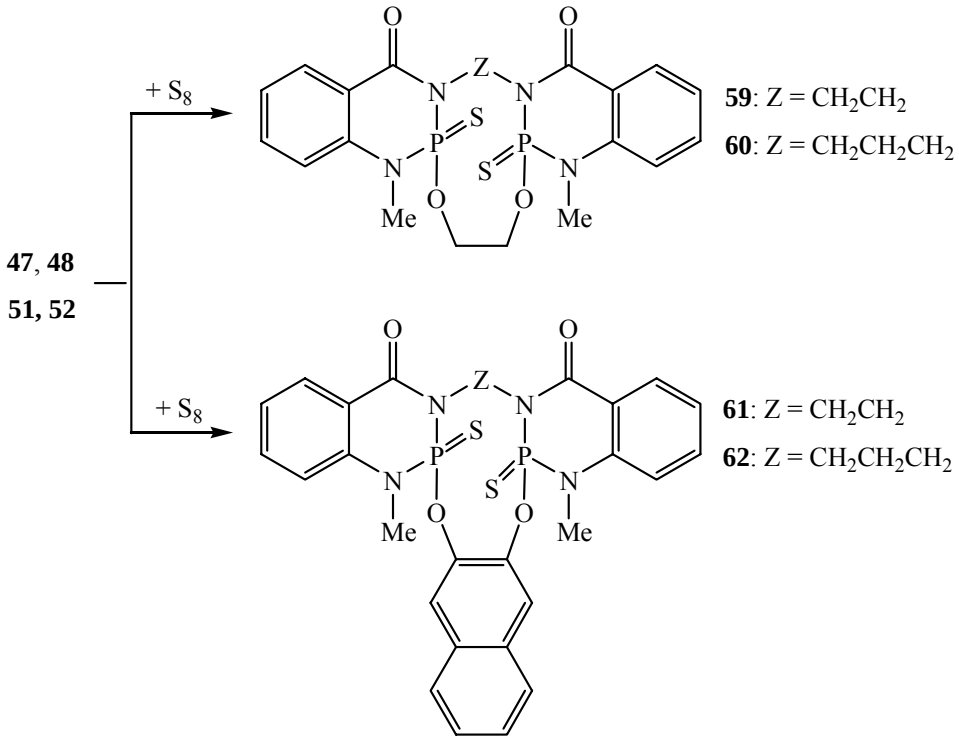
Condensation of **6** and **7** with several bistrimethylsilylethers lead to the formation of the new compounds **47-52** in moderate to high yield. Similar to the compounds **35-40**, all the compounds **47-52** displayed singlet signals in the ^{31}P-NMR spectra in $CDCl_3$ at room temperature. Once again, the ring-size in the new compounds does have significant influence on the chemical reactivity and physical properties such as melting points and solubility. In the solid state, the two halves of the central ten-membered ring in **51** are essentially identical, including bond lengths and bond angles. The six-membered heterocycles display a conformation in which the phosphorus atom lies outside the plane formed by the five other ring atoms.



Oxidation of compounds **47**-**52** lead to phosphoryl derivatives, **53**-**58**. Unlike the acyclic compounds, by which this kind of reaction usually take place spontaneously at room temperature, the polycyclic compounds need considerable long reaction time to be completely oxidized. They are all isolated as single conformer in high yield. Solid state structures of **54**, **56**, **57** and **58** have been analysed by single X-ray diffraction. The compound **54** forms host-guest complex with dichloromethane solvent molecule through P···O···H hydrogen bond.



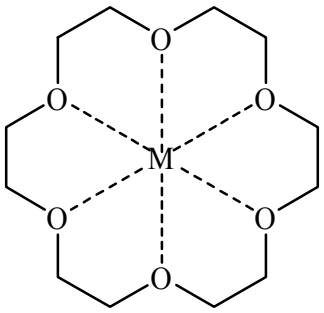
The reactions of **47**-**52** with elemental sulfur in refluxing toluene gave the corresponding sulfides **59**-**62**. No reaction occurred at room temperature. The bulkier spacer group -$OC_{10}H_6O$- may be responsible for the unusually high stability of **51** and **52**. All the compounds **59**-**62** display a singlet in the expected region in the ^{31}P-NMR spectra. Compounds **60** and **61** were analysed by single crystal X-ray diffraction. The bond lengths in both molecules differ only slightly, the geometry at the phosphorus atom is very different, due to the difference between the two bridging units, the ethylene and naphthylene groups.



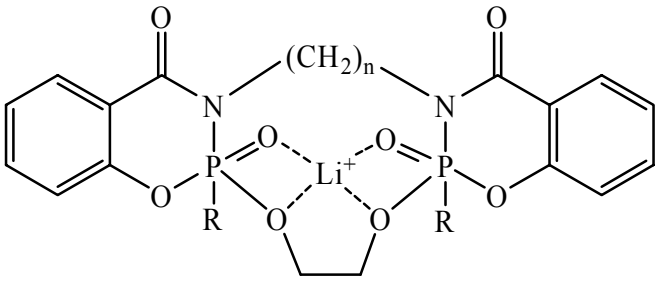
6.2. Future outlooks:

As this thesis is concerned only with fundamental studies about synthesis and reactivity, several points are of interest for further investigation, especially in the area of applications. The transition metal complexes formed from the bidentate ligands are potential candidates as catalysts, e.g. in asymmetric hydrogenation. Furthermore, all complexes studied in this thesis are from transition metals, main group elements such as Al, Ga are known to coordinate to both phosphorus and nitrogen atoms, this area is largely unexplored, neither in monodentate, nor in bidentate phosphorinanone systems.

The polycyclic compounds show close similarity to conventional crown and azacrown ethers, and they should be able to form host-guest complexes with both main group metals cations such as K^+, Ba^{2+} (host-guest system A). Utilizing this complexation-based process, these polycyclic systems may find useful applications in separation science. A reasonable coordination mode could be the oxygen atoms in the polycylic backone to small main group metal cations such as Li^+ or Na^+ (host-guest system B, see below).



host-guest system A



host-guest system B

7. Experimental

7.1. General Remarks

7.1.1. Experimental Conditions

All experiments were conducted with exclusion of air and moisture in sealed systems in a nitrogen atmosphere. Nitrogen was passed over heated BTS-catalyst and was dried over Sicapent and Silicagel. Solvents were purified and dried according to the usual methods [71, 72] and were stored over molecular sieve. Unless stated otherwise, all experiments were conducted in conventional glass apparatus, evacuated (0.1 mm Hg) and heated before use. Stirring of the reaction mixtures was carried out magnetically in all cases. "i. v." (in vacuo) refers to a pressure of 0.1 mm Hg, unless otherwise stated.

7.1.2. Methods Used for the Characterization of New Compounds

Melting Points (uncorrected): All melting points were determined in sealed capillaries on a Büchi 510 melting point apparatus.

NMR Spectroscopy: ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR-spectra were recorded, either in the NMR Laboratorium der Chemischen Institute der Technischen Universität Braunschweig, or in the Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig on a Bruker AC 200 instrument at the following frequencies:
^{1}H at 200.1 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz, ^{19}F at 188.3 MHz. Reference substances: TMS ext. (^{1}H); $CDCl_3$ int. (^{13}C); 85% H_3PO_4 ext. (^{31}P); $CFCl_3$ ext. (^{19}F). Chemical shifts (δ) are in ppm, coupling constants in Hertz (Hz). High-field shifts were given negative, low-field shifts positive signs. All NMR-spectra were recorded in $CDCl_3$ as a solvent unless stated otherwise.

Mass Spectra: The mass spectra were recorded on a Finnigan MAT 8430 instrument of the Mass Spektrometry Laboratory of der Chemischen Institute der Technischen Universität Braunschweig. The signal intensities are presented in %, relative to the base peak (100%).

Elemental Analyses: Elemental analyses were conducted at Analytisches Laboratorium des

Instituts für Anorganische und Analytische Chemie der Technischen Universität Braunschweig.

Infra-Red Spectra: Infra-red spectra were recorded on a Nicolet FT-IR-spectrometer at the Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig in $CHCl_3$ solutions.

Single-Crystal X-Ray Structure Analyses: The crystal structures were determined by Professor P. G. Jones and Dipl.-Chem. M. Freytag, Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig. The diffractometers Siemens R3 and Stoe STADI-4 were employed. For solution and refinement of the structures the program systems "SHELXTL PLUS-92" were used.

Starting Compounds: Transition metal complexes $Pt[COD]Cl_2$ (COD = cyclooctandiene), AuCl·[THT] (THT = tetrahydrothiofen), $Mo[NBD](CO)_4$ (NBD = norbadiene) are synthesed according to literature methods [73]. Other starting compounds were commercially available unless otherwise stated.

7.2. Description of the Experiments

Formation of Compound 5

A mixture of 2-hydroxy-1-naphthoic acid **1** (3.76 g, 20.00 mmol) and 1,1´-carbonyldiimidazole (3.24 g, 20.00 mmol) was refluxed in dry tetrahydrofuran (50 ml) for 1 h throughout under nitrogen. Ethylenediamine (0.60 g, 20.00 mmol) in dry tetrahydrofuran (10.0 ml) was added to the refluxing mixture in one portion. The reaction mixture was then refluxed overnight. The solvent was removed, the residue was washed with H_2O (3x10ml) and MeOH (3x10.0 ml), and dried i.v. at r.t. for 24 h.

Yield: 3.76 g (94%), colourless solid, m.p. 255°C.

$C_{24}H_{20}N_2O_4$ (400.43)

C 72.12 (calcd.: 72.00), H 5.23 (5.03), N 6.93 (7.00)%.

^{1}H-NMR (d6-DMSO)(ppm): δ = 8.24 (s, 2H, 2xO**H**), 7.74-7.12 (multiplets 12H, aromatic **H**), 3.80 (m, 4H, C**H**$_2$C**H**$_2$), 3.36 (s, 2H, 2xN**H**). EI-MS: m/z (%): 400 $[M]^+$ (90).

Formation of Compounds 8 and 9

General procedure:

Phosphorus trichloride (0.835g, 6.07 mmol) was added to a suspension of of **3** (1.00, 3.00 mmol)in 60 ml of toluene at room temperature. The resulting reaction mixture was then heated under reflux for 6 h. After removal of the solvent the solid residue was washed with 2x 15 ml of hexane and then dried i.v. The product was used without further purification.

8: Yield: 1.09 g (85%); m.p.: 188°C.

$C_{16}H_{12}Cl_2N_2O_4P_2$ (429.14)

Analysis: C 45.02 (calcd.: 44.78), H 3.11 (2.82), N 5.99 (6.53) %.

^{1}H-NMR: δ = 3.50-4.40 (m, 4H, C**H**$_2$C**H**$_2$), 6.90-8.05 (m, 8H, **H**aromatic), ^{31}P-NMR: δ = 143.76 (s). EI-MS: m/z (%): 428(<5) $[M]^+$ and other fragments, due to hydrolysis.

9: This product was obtained from 0.96 g (6.98 mmol) of PCl_3 and 1.07 g (3.41 mmol) of **4** in 60 ml of toluene, as described above, as a white powder after removal of the solvent.

Yield: 1.33 g (88%); m.p.: 192°C.

$C_{17}H_{14}Cl_2N_2O_4P_2$ (443.16)

Analysis: C 46.84 (calcd.: 46.07), H 3.92 (3.18), N 5.98 (6.32)%.

^{1}H-NMR: δ = 2.08 (m, 2H, CH_2C**H**$_2$$CH_2$), 2.90-3.80 (m, 4H, C**H**$_2$$CH_2$C**H**$_2$), 6.90-8.30 (m, 8H, **H**aromatic), ^{31}P-NMR: δ = 143.74 ppm. EI-MS: m/z (%): 442(<5) $[M]^+$ and other fragments, due to hydrolysis.

Formation of Compound 10

PCl_3 (2.71 g, 20.00 mmol) was added dropwise to a stirred suspension of **5** (4.00 g, 10.00 mmol) in 100 ml of toluene at 0°C. After completion of the addition, the resulting yellow suspension was refluxed for 6 hours. The resulting yellow solid was then collected by filtration. After washing with diethyl ether, the product was dried i. v.

Yield: 4.81 g (91%). m.p. >300°C.

$C_{24}H_{16}Cl_2N_2O_4P_2$ (529.26)

C 54.58 (calcd.: 54.47), H 3.02 (3.05), N 5.22 (5.29) %.

^{1}H-NMR (ppm): δ = 3.00 and 4.00 (2 multiplets, 4H, 2H, C**H**$_2$C**H**$_2$), 6.80-8.50 (m, 12H,**H**aromatic). ^{31}P-NMR (ppm): δ = 141.02 (s). EM m/z (%): 527 $[M]^+$ (20).

Formation of Compounds 11 - 13

The preparation of **11** is described as a typical example:

To a suspension of a freshly prepared sample of **6** (4.55 g, 10.00 mmol) in 50 ml dichloromethane, Me_2NSiMe_3 (2.36 g, 20.00 mmol) was added at 0°C in one portion. The reaction mixture was allowed to warm up to r.t. and stirred for 15 min. Subsequently, the solvent and volatile compounds were removed i.v.. The residue was recrystallized from diethyl ether and dichloromethane to give the product.

11: Yield: 3.87g (82%), m.p >300°C.

$C_{22}H_{30}N_6O_2P_2$ (472.47)

Analysis: C 56.02 (calcd.: 55.93), H 6.62 (6.40), N 17.21 (17.79).

^{1}H-NMR: δ = 2.27 (t, 18H, 2 x N(C**H**$_3$)$_2$, 2 x N(C**H**$_3$), ^{3}J(HH) = 7.03Hz), 3.10-3.80(m, 4H, NC**H**$_2$C**H**$_2$N), 7.09-8.05(m, 12H, **H**aromatic), ^{13}C-NMR: no ^{13}C-NMR spectrum could be obtained for this compound because of its low solubility in common solvents. ^{31}P-NMR: δ = 92.60 (s), δ = 92.41 (s). EI-MS: m/z (%): 472(10) $[M]^+$, 428(80) $[M- (CH_3)_2N]^+$.

12: From 4.55 g (10.00 mmol) of **6** and 3.18g (20.00mmol) of $Me_3SiN(CH_2CH_2)_2O$

Yield: 4.50g (81%), m.p >300°C.

$C_{26}H_{34}N_6O_4P_2$ (556.64)

Analysis: C 56.42 (calcd.: 56.11), H 6.62 (6.16), N 14.91 (15.10), O 11.97(11.50) %

^{1}H-NMR: δ = 3.01 (m, 16H, 2 x N(C**H**$_2$C**H**$_2$)$_2$O), 2.27 (t, 6H, 2 x N(C**H**$_3$), ^{3}J(HH) = 7.03Hz), 3.05-4.15(m, 4H,NC**H**$_2$C**H**$_2$N), 7.10-8.02(m, 12H, Haromatic), ^{13}C-NMR: no ^{13}C-NMR spectrum could be obtained for this compound, due to its low solubility in common solvents. ^{31}P-NMR: δ = 87.48 (s), δ = 87.16 (s). EI-MS: m/z(%): 556(10) $[M]^+$, 470 (80) $[M-N(C_2H_4)_2O]^+$.

13: From 5.50 g (10.00 mmol) of **8** and 3.18g (20.00mmol) of $Me_3SiN(CH_2CH_2)_2O$

Yield: 4.50g (81%), m.p >300°C.

$C_{24}H_{28}N_4O_6P_2$ (530.64)

Analysis: C 56.42 (calcd.: 56.11), H 6.62 (6.16), N 14.91 (15.10), O 11.97(11.50) %

^{1}H-NMR: δ = 3.01 (m, 16H, 2 x N(C**H**$_2$C**H**$_2$)$_2$O), 3.05-4.15(m, 4H,NC**H**$_2$C**H**$_2$N), 7.10-8.02(m, 12H, Haromatic), ^{13}C-NMR: no ^{13}C-NMR spectrum could be obtained for this

compound, due to its low solubility in common solvents. ^{31}P-NMR: δ = 108.48. EI-MS: m/z(%): 530(10) $[M]^+$.

Preparation of compounds **14-17**

The preparation of **14** is described as a typical example. Compounds 1**5**, 1**6** and 1**7** are prepared, using the same method as described for **14**, from one equivalent of **10** (5.29g, 10.00 mmol) and two equivalents of the corresponding trimethylsilylamines.

To a suspension of a freshly prepared sample of **10** (5.29 g, 10.00 mmol) in 50 ml of dichloromethane, Me_2NSiMe_3 (2.34 g, 20.00 mmol) was added at 0°C in one portion. The reaction mixture was allowed to warm up to r.t. and was stirred for 15 min. Subsequently, the solvent and volatile compounds were removed i.v.. The residue was recrystallized from diethyl ether and dichloromethane to give the product **14**.

14: Yield: 4.42 g (81%); m. p. 180°C.

$C_{28}H_{28}N_4O_4P_2$ (546.50)

Analysis: C 61.84 (calcd.: 61.54), H 5.62 (5.16), N 9.81 (10.25) %.

^{1}H-NMR (one isomer): δ = 2.52 (d, 12H, ^{3}J(PH) = 9.34Hz, 2 x N(C**H**$_3$)$_2$), 3.05-4.15 (m, 4H,C**H**$_2$C**H**$_2$), 7.08-9.57 (m, 12H, **H**aromatic), ^{31}P-NMR: δ = 109.18 (s), δ = 109.29 (s). EI-MS: m/z (%): 546 (30) $[M]^+$, 530 (80) $[M- C_2H_7N]^+$.

15: From 5.29 g (10.00 mmol) of **10** and 2.90g (20.00mmol) of Me_3SiNEt_2.

Yield: 4.93 g (82%); m.p 146°C.

$C_{32}H_{36}N_4O_4P_2$ (602.6098)

Analysis: C 64.02 (calcd.: 63.78), H 6.62 (6.02), N 8.81 (9.30)%.

^{1}H-NMR(one isomer): δ = 0.85 (t, 12H, 2 x N(CH$_2$C**H**$_3$)$_2$, ^{3}J(HH) = 7.02Hz), 2.85-3.10 (m, 8H, 2 x N(C**H**$_2$CH$_3$)$_2$), 3.86-4.07 (m, 4H, NC**H**$_2$C**H**$_2$N), 7.09-9.60 (m, 12H, **H**aromatic), ^{31}P-NMR: δ = 106.72 (s), δ = 107.99 (s). EI-MS: m/z (%): 602 (40) $[M]^+$, 530 (80) $[M-C_4H_{10}N]^+$.

16: From 5.29 g (10.00 mmol) of **10** and 3.18g (20.00mmol) of $Me_3SiN(CH_2CH_2)_2O$

Yield: 5.160 g (82%); m.p. 240°C.

$C_{32}H_{32}N_4O_6P_2$ (630.57)

Analysis: C 61.02 (calcd.: 60.95), H 5.62 (5.12), N 8.71 (8.89)%.

^{1}H-NMR (one isomer): δ = 3.00 (m, 16H, 2 x N(C**H**$_2$C**H**$_2$)$_2$O), 3.05-4.15 (m, 4H, NC**H**$_2$C**H**$_2$N), 7.12-9.88 (m, 12H, **H**aromatic), ^{31}P-NMR: δ = 102.03 (s), δ = 101.87 (s). EI-MS: m/z (%): 630 (10) $[M]^+$, 543 (60) $[M- C_4H_9NO]^+$.

17: From 5.29 g (0.01 mmol) of **10** and 3.54g (20.00mmol) of $Me_3SiNHPh$

Yield: 5.20g (81%), m.p 190°C.

$C_{36}H_{28}N_4O_4P_2$ (642.59)

Analysis: C 67.84 (calcd.: 67.29), H 4.62 (4.39), N 8.31 (8 .72)%.

^{1}H-NMR: δ = 3.40-4.70 (m, 4H,NC**H**$_2$C**H**$_2$N), 6.00 (2H, broad signal, 2x N**H**), 7.02-8.90 (m, 22H, **H**aromatic), ^{31}P-NMR: δ = 99.11 (s), δ = 94.84 (s). EI-MS: m/z (%): 642 (10) $[M]^+$, 93 (100) $[C_6H_5NH+H]^+$.

*Preparation of compound **18***

Compound **11** (0.11 g, 0.20 mmol) was dissolved in 15 ml of dichloromethane. To this solution hexafluoroacetone (about 0.50g, 3.00 mmol, excess) was condensed at -196°C. The reaction mixture was allowed to warm up to room temperature within 1 h and then stirred for 4 d at r.t. After removal of the solvents and other volatile compounds the solid residue was washed with 2 x 5 ml diethyl ether to give the product **18**.

Yield: 0.16g (74%), m.p 147°C.

$C_{34}H_{30}F_{24}N_6O_6P_2$ (1136.56)

Analysis: C 36.01 (calcd.: 35.93), H 2.92 (2.66), N 7.21 (7.39)

^{1}H-NMR: d = 2.51 (d, 18H, ^{3}J(PH) = 10.63Hz, 2 x N(C**H**$_3$), 2 x N(C**H**$_3$)$_2$), 3.70-4.18 (m, 4H,NC**H**$_2$C**H**$_2$N), 7.02-8.27(m, 12H, **H**aromatic), no ^{13}C NMR spectrum was obtained. ^{19}F-

NMR: δ= -76.05 (m, 6F, $OC(CF_3)_2$, axial), -68.76 (m, 6F, $OC(CF_3)_2$, aquatorial), ^{31}P-NMR: δ = -28.96 (s), δ = -30.53 (s). EI-MS: m/z (%): 1136 (10) $[M]^+$.

*Preparation of compounds **19-22***

The preparation of **19** is described as a typical example. Compounds **20**, **21** and **22** are prepared using the same method.

Compound **14** (0.11 g, 0.20 mmol) was dissolved in 15 ml of dichloromethane. To this solution hexafluoroacetone (ca. 0.50g, 3.00 mmol, excess) was condensed at -196°C. The reaction mixture was allowed to warm up to room temperature within 1 h and then stirred for 4 d at r.t. After removal of the solvents and other volatile compounds the solid residue was washed with 2 x 5 ml diethyl ether to give the product **19**.

19: Yield: 0.18 g (76%); m.p 182°C.

$C_{40}H_{28}F_{24}N_4O_8P_2$ (1,210.59)

Analysis: C 40.01 (calcd.: 39.69), H 2.62 (2.33), N 4.21 (4.63)%.

^{1}H-NMR: δ = 2.50 (d, 12H, ^{3}J(PH) = 10.63Hz, 2 x $N(C\mathbf{H}_3)_2$), 4.05-4.65 (m, 4H,$NC\mathbf{H}_2C\mathbf{H}_2N$), 7.02-9.69 (m, 12H, **H**aromatic). ^{19}F-NMR: δ = -70.50 (m, 6F, $OC(CF_3)_2$, axial), -67.80 (m, 6F, $OC(CF_3)_2$, aquatorial), ^{31}P-NMR: δ = -47.12 (s), -47.89 (s). EI-MS: m/z (%): 1210 (10) $[M]^+$, 1166 (30) $[M- N(CH_3)_2]^+$.

20: From 0.12g (0.20mmol) of **15** and hexafluoroacetone (ca. 0.50g, 3.00 mmol, excess).

Yield: 0.20g (78%), m.p: 222°C.

$C_{44}H_{36}F_{24}N_4O_8P_2$ (1,266.70)

Analysis: C 42.02 (calcd.: 41.72), H 2.99 (2.86), N 4.11 (4.42)%.

^{1}H-NMR: δ = 0.90 (t, 12H, 2 x $N(CH_2C\mathbf{H}_3)_2$, ^{3}J(HH) = 7.02Hz), 2.85-3.10 (m, 8H, 2 x $N(C\mathbf{H}_2CH_3)_2$), 3.10-3.87 (m, 4H, $NC\mathbf{H}_2C\mathbf{H}_2N$), 7.09-9.02 (m, 12H, **H**aromatic), ^{19}F-NMR: δ = -72.50 (m, 6F, $OC(CF_3)_2$, axial), -69.10 (m, 6F, $OC(CF_3)_2$, aquatorial), ^{31}P-NMR: δ = -43.81(s), EI-MS: m/z (%): 1266 (20) $[M]^+$, 1194(80) $[M- NC_2H_5]^+$.

21: From 0.12 g (0.20 mmol) of **16** and and hexafluoroacetone (ca. 0.50g, 3.00 mmol, excess).

Yield: 0.19 g (75 %), m.p 160°C.

$C_{44}H_{32}F_{24}N_4O_{10}P_2$ (1,294.67)

Analysis: C 41.02 (calcd.: 40.82), H 2.62 (2.49), N 4.11 (4.33) %.

^{1}H-NMR(one isomer): δ = 3.0 (m, 16H, 2 x N(CH_2CH_2)$_2$O), 3.05-4.15(m, 4H,NC**H**$_2$C**H**$_2$N), 7.11-9.49 (m, 12H, **H**aromatic), ^{19}F-NMR: δ = -73.48 (m, 6F, OC(CF_3)$_2$, axial), -68.19(m, 6F, OC(CF_3)$_2$, aquatorial). ^{31}P-NMR: δ = -46.73 (s), δ = -46.98 (s). EI-MS: m/z (%): 1294 (20) $[M]^+$, 1208 (60) $[M- C_4H_8NO]^+$.

22: From 0.13 g (0.20mmol) of **17** and and hexafluoroacetone (ca. 0.50g, 3.00 mmol, excess).

Yield: 0.20g (78%), m.p 188°C.

$C_{48}H_{28}F_{24}N_4O_6P_2$ (1,306.68)

Analysis: C 44.84 (calcd.: 44.12), H 2.62 (2.16), N 4.01 (4.29) %.

^{1}H-NMR: δ = 3.70-4.60 (m, 4H, NC**H**$_2$C**H**$_2$N), 7.10-9.30 (m, 12H, **H**aromatic), ^{13}C-NMR: no ^{13}C-NMR spectrum could be obtained for this compound because of its low solubility in common solvents. ^{19}F-NMR: δ = -75.10 (m, 6F, OC(CF_3)$_2$, axial), -69.10 (m, 6F, OC(CF_3)$_2$, aquatorial). ^{31}P-NMR: δ = -57.23 (s), EI-MS: m/z (%): 642 (10) $[M]^+$, 93 (100) $[C_6H_5NH+H]^+$.

*Preparation of compounds **23-25***

The preparation of **23** is described as a typical example.

To a solution of **12** (0.11g, 0.20 mmol) in 40ml dichloromethane (0.10 g, 0.40mmol) tetrachloro-orthobenzoquinone was added at room temperature. The reaction was stirred for 1 day and then the solvent was removed i.v.. The product was washed with 2x 5ml diethyl ether to give the pure product.

23: Yield: 0.09 (44%), m.p >230°C.

$C_{38}H_{34}Cl_8N_6O_8P_2$ (1,048.29)

Analysis: C 43.92 (calcd.: 43.54), H 3.62 (3.27), N 7.91 (8.02), O 12.97(12.21) %

^{1}H-NMR, ^{13}C-NMR: no ^{13}C-NMR and ^{1}H-NMR spectrum were obtained for this compound because of its low solubility in common solvents. ^{31}P-NMR: δ = -31.52 (s), EI-MS: m/z(%): 1,048(10) $[M]^+$, 962(80) $[M- N(C_2H_4)_2O]^+$.

24: From 0.10 g (0.20 mmol) of **14** and tetrachloro-orthobenzoquinone (TOB).

Yield: 0.09 g (45%), m.p. 255°C.

$C_{40}H_{28}Cl_8N_4O_8P_2$ (1,038.26)

C 46.32 (calcd.: 46.27), H 2.78 (2.72), N 5.37 (5.40) %.

^{1}H-NMR: δ = 2.52 (d, 12H, ^{3}J(PH) = 9.34Hz, 2 x N(C**H**$_3$)$_2$), 4.04-4.27 (m, 4H,C**H**$_2$C**H**$_2$), 7.01-8.80 (m, 12H, **H**aromatic). ^{31}P-NMR: δ = -43.21 (s), δ = -43.87 (s). EI-MS: m/z (%): 1034 (60) $[M]^+$, 990 (80) $[M-(CH_3)_2N]^+$. ^{13}C-NMR: no ^{13}C-NMR and spectrum were obtained for this compound because of its low solubility in common solvents.

25: Using the same method as described above from 0.13 g (0.20 mmol) of **16** and tetrachloro-orthobenzoquinone (TOB).

Yield: 0.10 g (46 %), m.p 231°C.

$C_{44}H_{32}Cl_8N_4O_{10}P_2$ (1,122.33)

C 47.12 (calcd.: 47.09), H 2.92 (2.87), N 4.85 (4.99) %.

^{1}H-NMR: δ = 3.00 (m, 16H, 2 x N(CH_2CH_2)$_2$O), 3.05-4.15 (m, 4H,NC**H**$_2$C**H**$_2$N), 7.10-9.81 (m, 12H, **H**aromatic), ^{31}P-NMR: δ = -44.60 (s), δ = -46.73 (s). EI-MS: m/z (%): 1,118 (10) $[M]^+$, 1,032 (60) $[M- C_4H_8NO]^+$.

*Preparation of compounds **26-31***

The preparation of **26** is described as a typical example.

To a solution of **13** (0.11 g, 0.20mmol) in 20 ml of dichloromethane Pt[COD]Cl_2 (0.08 g, 0.20 mmol) in 10ml dichloromethane was added at 0°C. The reaction mixture was allowed to warm up to room temperature and then stirred for 30 min. After removal of the solvent the solid residue was washed with 2 x 15 ml of diethyl ether and then dried i.v.

26: Yield: 0.57 g (72%); m.p.: >300°C.

$C_{24}H_{28}Cl_2N_4O_6P_2Pt$ (796.54)

Analysis: C 36.68 (calcd.: 36.19), H 4.91 (3.54), N 6.86 (7.03), O 12.99 (12.05)%.

^{1}H-NMR: δ = 1.41-2.82 (m, 16H, 2 x N(CH_2CH_2)$_2$O)δ = 2.91-4.81(m, 4H, NCH_2CH_2N), 7.08-7.90 (m, 8H, Haromatic), ^{13}C-NMR: no ^{13}C-NMR was obtained due to the poor solubility of **26** in the common solvents. ^{31}P-NMR: δ = 76.65 (t, ^{1}J(PPt) = 2565 Hz), 75.52 (t, ^{1}J(PPt) = 2607 Hz) EI-MS: m/z (%): 796 (10) $[M]^+$.

27: From 0.11 g (0.20 mmol) of **12** and Pt[COD]Cl_2 (0.08g, 0.20 mmol)

Yield: 0.58 g (71%); m.p.: >300°C.

$C_{32}H_{32}Cl_2N_4O_6P_2Pt$ (822.54)

Analysis: C 38.08 (calcd.: 37.97), H 4.91 (4.17), N 10.06 (10.22), O 7.99 (7.78)%.

^{1}H-NMR: δ = 1.40-2.80 (x, 16H, 2 x N(CH_2CH_2)$_2$O), 3.09 (d, 6H, 2 x NCH_3, ^{2}J(PH) 12.02Hz), δ= 2.90-4.80 (m, 4H, NCH_2CH_2N), 7.08-7.96 (m, 12H, Haromatic), ^{13}C-NMR: no ^{13}C-NMR coulde be obtained due to the poor solubility of **27** in the common solvents. ^{31}P-NMR: δ = 68.77 (t, ^{1}J(PPt) = 2559 Hz), 66.64 (t, ^{1}J(PPt) = 2459 Hz)

EI-MS: m/z (%): 822 (10) $[M]^+$.

28: This compound was obtained as a mixture of two conformers from 0.11 g (0.20 mmol) of **14** and Pt[COD]Cl_2 (0.08g, 0.20 mmol) using the same method as described above for the preparation of **26**. Crystals suitable for X-ray analysis were obtained by cooling a CH_2Cl_2/Et_2O solution at –20°C overnight.

Yield: 0.13 g (75%); m.p.: 271°C.

$C_{28}H_{28}Cl_2N_4O_4P_2Pt$ (812.50)

Analysis: C 41.78 (calcd.: 41.39), H 3.91 (3.47), N 6.26 (6.90)%.

^{1}H-NMR: δ = 3.10 (d, 12H, ^{3}J(PH) = 11.81Hz, 2 x N(C**H**$_3$)$_2$), 4.78-5.51(m, 4H,C**H**$_2$C**H**$_2$), 7.02-9.47(m, 12H, **H**aromatic), ^{13}C-NMR: δ = 38.30 (d, 4C, ^{2}J(PC) = 4.06Hz, 2 x N(**C**H_3)$_2$), 41.82(d, ^{2}J(PC) = 3.57Hz, N**C**H_2**C**H_2N), 107.22-137.01(m, other aromatic **C** atoms), 162.81 (d, ^{2}J(PC) = 4.56Hz, **C**(:O)NP), ^{31}P-NMR: δ = 78.14 (t, ^{1}J(PPt) = 2585.8 Hz), FAB-MS: m/z (%): 812 (20) $[M]^+$, 777 (80) $[M\text{-}HCl]^+$.

29: This compound was prepared as a mixture of two conformers from 0.12 g (0.20 mmol) of **15** and Pt[COD]Cl_2 (0.08g, 0.20 mmol) using the same method as described above by the preparation of **26**.

Yield: 0.13g (73%); m.p.: 285°C.

$C_{32}H_{36}Cl_2N_4O_4P_2Pt$ (868.61)

Analysis: C 44.78 (calcd.: 44.25), H 4.91 (4.18), N 6.06 (6.45)%.

^{1}H-NMR (one conformer): δ = 0.82 (t, 12H, 2 x N($CH_2C\mathbf{H}_3)_2$, ^{3}J(HH) = 7.36Hz), 2.91-3.77 (m, 8H, 2 x N($C\mathbf{H}_2CH_3)_2$), 4.37-4.92 (m, 4H, N$C\mathbf{H}_2C\mathbf{H}_2$N), 7.01-9.43 (m, 12H, **H**aromatic), ^{31}P-NMR: δ = 78.59 (s, ^{1}J(PPt) = 2576.81 Hz), 78.27 (s, ^{1}J(PPt) = 2602.52 Hz). FAB-MS: m/z (%): 868 (10) $[M]^+$, 833 (80) $[M\text{-}HCl]^+$. ^{13}C-NMR: no ^{13}C-NMR coulde be obtained due to the poor solubility of **29** in the common solvents.

30: This compound was prepared from **16** (0.13 g, 0.20 mmol) and Pt[COD]Cl_2 (0.08g, 0.20 mmol) using the same method as described above for the preparation of **26**. Crystals suitable for an X-ray study were obtained by cooling a dichloromethane-diethyl ether solution at –20°C overnight.

Yield: 0.67 g (75%); m.p.: >300°C.

$C_{32}H_{32}Cl_2N_4O_6P_2Pt$ (896.57)

Analysis: C 43.08 (calcd.: 42.87), H 3.91 (3.60), N 6.06 (6.25)%.

^{1}H-NMR (one isomer): δ = 1.40-2.80 (m, 16H, 2 x N($C\mathbf{H}_2C\mathbf{H}_2)_2$O), δ = 2.90-4.80 (m, 4H, N$C\mathbf{H}_2C\mathbf{H}_2$N), 7.10-9.80 (m, 12H, **H**aromatic), ^{31}P-NMR: δ = 76.34 (t, ^{1}J(PPt) = 2605 Hz). EI-MS: m/z (%): 896 (10) $[M]^+$, 861 (20) $[M\text{-}HCl]^+$. ^{13}C-NMR: no ^{13}C-NMR coulde be obtained due to the poor solubility of **30** in the common solvents

31 This compound was prepared as a mixture of two conformers from 0.12 g (0.20 mmol) of **17** and Pt[COD]Cl_2 (0.08g, 0.20 mmol) using the same method as described above by the preparation of **26**.

Yield: 0.65 g (72%); m.p.: >300°C.

$C_{36}H_{28}Cl_2N_4O_4P_2Pt$ (908.59)

Analysis: C 48.08 (calcd.: 47.58), H 3.71 (3.08), N 5.96 (6.17)%.

^{1}H-NMR: δ = 3.40-4.70 (m, 4H,N$C\mathbf{H}_2C\mathbf{H}_2$N), 6.00 (2H, broad signal, 2x N**H**), 7.02-8.90 (m, 22H, **H**aromatic), ^{31}P-NMR: δ = 75.52 (s). EI-MS: m/z (%): 908 (10) $[M]^+$. ^{13}C-NMR: no ^{13}C-NMR coulde be obtained due to the poor solubility of **31** in the common solvents

*Preparation of compounds **32-34***

The preparation of **32** is described as a typical example.

To a solution of **11** (0.08 g, 0.20 mmol) in 20 ml of dichloromethane (NBD)$Mo(CO)_4$ (0.06 g, 0.20 mmol) in 10ml of dichloromethane was added at 0°C. The reaction mixture was allowed to warm up to room temperature and then stirred for 30 min. After removal of the solvent the solid residue was washed with 2 x 15 ml of diethyl ether and then dried i.v.

32:

Yield: 1.05g (77%), m.p >300°C.

$C_{26}H_{30}N_6O_6P_2Mo$ (680.41) Analysis: C 45.02 (calcd.: 45.89), H 4.62 (4.44), N 12.21 (12.35)

^{1}H-NMR: δ = 2.27 (t, 18H, 2 x N(C**H**$_3$)$_2$, 2 x N(C**H**$_3$), ^{3}J(HH) = 7.03Hz), 3.10-3.80(m, 4H, NC**H**$_2$C**H**$_2$N), 6.87-8.26(m, 12H, **H**aromatic), ^{13}C-NMR: this was not obtained for **32** because of its low solubility in common solvents. ^{31}P-NMR: δ = 92.60(s), δ = 149.37(s), 147.33(s). EI-MS: m/z(%): 680(10) [M^+], 428(80) [M- $(CH_3)_2NMo(CO)_4$]$^+$.

33: This compound was prepared from **12** (0.11 g, 0.20 mmol) and 0.60g, 0.20mmol [NBD]$Mo(CO)_4$ using the same method as described above for the preparation of **32**.

Yield: 0.15g (76%); m.p.: >300°C.

$C_{30}H_{34}MoN_6O_8P_2$ (764.52)

Analysis: C 47.68 (calcd.: 47.13), H 4.91 (4.48), N 10.06 (10.99).

^{1}H-NMR: δ = 3.01(m, 16H, 2 x N(C**H**$_2$C**H**$_2$)$_2$O), 2.27 (t, 6H, 2 x N(C**H**$_3$), ^{3}J(HH) = 7.03Hz), 3.05-4.15(m, 4H,NC**H**$_2$C**H**$_2$N), 7.10-8.02(m, 12**H**, Haromatic), ^{13}C-NMR: not obtained due to the poor solubility of the compound. ^{31}P-NMR: δ = 147.74 (s); EI-MS: m/z (%): 764 (20) [M]$^+$.

34: To a solution of **12** (0.11g, 0.20 mmol) in 20 ml of dichloromethane THF·$AuCl_2$ (0.13 g, 0.40 mmol) in 10ml dichloromethane was added at 0°C in the dark. The reaction mixture was allowed to warm up to room temperature and then stirred for 30 min. After removal of the solvent the solid residue was washed with 2 x 15 ml of diethyl ether and then dried i.v.

m.p.: > 300°C.

$C_{26}H_{34}Au_2Cl_2N_6O_4P_2$ (1,021.38)

Analysis: C 30.68 (calcd.: 30.57), H 3.91 (3.36), N 8.06 (8.23).

^{1}H-NMR: δ = 3.01(m, 16H, 2 x N(CH_2CH_2)$_2$O), 2.27 (t, 6H, 2 x N(CH_3), ^{3}J(HH) = 7.03Hz), 3.05-4.15(m, 4H,NCH_2CH_2N), 7.10-8.02(m, 12H, Haromatic), ^{13}C-NMR: not obtained due to the poor solubility of **34**. ^{31}P-NMR: δ = 93.92 (s), 93.29 (s);

*Preparation of compounds **35-40***

The preparation of **35** is described as a typical example.

Bis(trimethylsiloxy)ethane (0.43 g; 2.09 mmol) was added to a suspension of 0.90g (2.10 mmol) of freshly prepared **3** in 60 ml of dichloromethane (when react with compound **4**, the reaction was a clear solution). The mixture was stirred for 4d (during this time the ^{31}P-NMR signal for the starting compound **3** disappeared completely). After removal of the solvent, the product was obtained by recrystallization from dichloromethane/diethyl ether.

35: Yield: 0.489g (56%); m.p.: 172°C.

$C_{18}H_{16}N_2O_6P_2$ (418.28)

Analysis: C 51.89 (calcd.: 51.69), H 4.01 (3.86), N 6.56 (6.70)%.

^{1}H-NMR: δ = 3.29-4.36 (m, 8H, C**H**$_2$C**H**$_2$), 6.85-7.99 (m, 8H, **H**aromatic), ^{31}P-NMR: δ = 133.20 (s). ^{13}C-NMR: not obtained due to the poor solubility of the compound. EI-MS: m/z(%): 418(80) $[M]^+$, 374(38) $[M\text{-}OCH_2CH_2]^+$.

36: From 1.33g (3.00ml) of **4** and 0.62g (3.00ml) of bis(trimethylsiloxy)benzene

Yield: 0.700g (54%); m.p.: 171°C.

$C_{19}H_{18}N_2O_6P_2$ (432.31)

Analysis: C 53.01 (calcd.: 52.79), H 4.85 (4.20), N 6.06 (6.48)%.

^{1}H-NMR: δ = 2.00 (m, 2H, $CH_2C\mathbf{H}_2CH_2$), 3.30-4.10 (m, 8H, N**H**$_2$CH$_2$C**H**$_2$N and O**H**$_2$C**H**$_2$O), 6.80-8.10 (m, 8H, **H**aromatic), ^{13}C-NMR: not obtained due to the poor solubility of the compound. ^{31}P-NMR: δ = 127.22 (s), 122.16(s). EI-MS: m/z(%): 432(5) $[M]^+$.

37: From 0.88g (2.05ml) of **3** and 0.51g (2.02ml) of bis(trimethylsiloxy) benzene

Yield: 0.499g (52%); m.p.: 172°C.

$C_{22}H_{16}N_2O_6P_2$ (466.33)

Analysis: C 57.01 (calcd.: 56.66), H 3.95 (3.46), N 5.86 (6.01)%.

^{1}H-NMR: δ = 3.30-4.50 (m, 4H, C**H**$_2$C**H**$_2$), 6.60-8.10 (m, 12H, **H**aromatic), ^{13}C-NMR: not obtained due to the poor solubility of the compound. ^{31}P-NMR: δ = 125.69 (s). EI-MS: m/z(%): 466(30) $[M]^+$, 374(36) $[M\text{-}OC_6H_4]^+$.

38: From 0.45g (1.02ml) of **4** and 0.25g (1.00ml) of bis(trimethylsiloxy) benzene

Yield: 0.215g (44%); m.p.: 173°C.

$C_{23}H_{18}N_2O_6P_2$ (480.34)

Analysis: C 58.01 (calcd.: 57.51), H 3.95 (3.78), N 5.06 (5.83)%.

^{1}H-NMR: δ = 2.10 (m, 4H, $CH_2C\mathbf{H}_2CH_2$), 3.10-4.50 (m, 4H, $C\mathbf{H}_2CH_2C\mathbf{H}_2$), 6.70-8.20 (m, 12H, **H**aromatic), ^{13}C-NMR: not obtained due to the poor solubility of the compound. ^{31}P-NMR: δ = 118.88 (s), 118.39(s) EI-MS: m/z(%): 478(25) $[M]^+$, 386 (30) $[M\text{-}OC_6H_4]^+$.

39: From 1.07g (2.50ml) of **3** and 0.76g (2.50ml) of bis(trimethylsiloxy)naphthalene

Yield: 0.697g (54%); m.p.: 173°C.

$C_{26}H_{18}N_2O_6P_2$ (516.39)

Analysis: C 60.91 (calcd.: 60.48), H 3.95 (3.51), N 5.02 (5.42)%.

^{1}H-NMR: δ = 3.30-4.60 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2$), 7.10-8.10 (m, 14H, **H**aromatic), ^{13}C-NMR: not obtained due to the poor solubility of the compound. ^{31}P-NMR: δ = 124.58 (s). EI-MS: m/z(%): 516 (20) $[M]^+$, 374 (30) $[M\text{-}OC_{10}H_6]^+$.

40: From 1.11g (2.50ml) of **4** and 0.76g (2.50ml) of bis(trimethylsiloxy) naphthalene

Yield: 0.530g (40%); m.p.: 174°C.

$C_{27}H_{20}N_2O_6P_2$ (530.41)

Analysis: C 61.91 (calcd.: 61.14), H 4.05 (3.80), N 4.92 (5.28)%.

^{1}H-NMR: δ = 2.10 (m, 2H, $CH_2C\mathbf{H}_2CH_2$), 3.20-4.50 (m, 4H, $C\mathbf{H}_2CH_2C\mathbf{H}_2$), 7.20-8.10 (m, 14H, **H**aromatic), ^{13}C-NMR: not obtained due to the poor solubility of the compound. ^{31}P-NMR: δ = 122.13 (s), 120.33 (s). EI-MS: m/z(%): 530 (20) $[M]^+$, 386 (30) $[M\text{-}OC_{10}H_6]^+$.

*Preparation of compounds **41-46***

The preparation of **41** is described as a typical example.

To a solution of 0.418g (1.00mmol) of **35** in 60 ml of dichloromethane was added 1.0 g (5.00mmol) of $(NH_2)_2C(:O)\cdot H_2O_2$ (excess) at room temperature. The reaction mixture was stirred for 4 h and was then filtered. The filtrate was washed with 2x10ml of water and then dried over $MgSO_4$ overnight. After filtration and removal of the solvent the product was obtained as a colourless solid.

41: Yield: 0.382g (85%); m.p.: 262°C.

$C_{18}H_{16}N_2O_8P_2$ (450.28)

Analysis: C 48.89 (calcd.: 48.01), H 3.91 (3.58), N 6.06 (6.22)%.

^{1}H-NMR: δ = 3.60-4.78 (m, 8H, C**H**$_2$C**H**$_2$), 6.80-8.10 (m, 8H, **H**aromatic), ^{13}C-NMR: δ = 162.52(d, ^{2}J(PC) = 7.01Hz, **C**(:O)NP), 150.07(d, ^{2}J(PC) = 5.84Hz, **C**-O-P), 135.80-113.80 (m, other aromatic **C** atoms), 67.64 (dd, ^{2}J(PC) = ^{3}J(PC) = 6.04Hz, P-O**C**H$_2$), 43.56 (dd, ^{2}J(PC) = ^{3}J(PC) = 3.05Hz, P-N**C**H$_2$); ^{31}P-NMR: δ = -1.66(s). EI-MS: m/z(%): 450(58) $[M]^+$, 406(20) $[M\text{-}OCH_2CH_2]^+$.

42: From 0.432 g (1.00 mmol) of **36** and 1.0 g (5.00mmol) $(NH_2)_2C(:O)\cdot H_2O_2$.

Yield: 0.404g (87%); m.p.: 192°C.

$C_{19}H_{18}N_2O_8P_2$ (464.31)

Analysis: C 49.67 (calcd.: 49.15), H 4.11 (3.91), N 5.91 (6.03)%.

^{1}H-NMR: δ = 2.16 (m, 2H, CH$_2$C**H**$_2$CH$_2$), 3.60-4.80 (m, 8H, NC**H**$_2$CH$_2$C**H**$_2$N and OC**H**$_2$C**H**$_2$O), 6.90-8.30 (m, 8H, **H**aromatic), ^{13}C-NMR: δ = 162.43 (d, ^{2}J(PC) = 7.05Hz, **C**(:O)NP), 149.93 (d, ^{2}J(PC) = 5.73Hz, **C**-O-P), 135.61-116.89 (m, other aromatic **C** atoms), 67.17 (dd, ^{2}J(PC) = ^{3}J(PC) = 6.07Hz, P-O**C**H$_2$), 39.98 (dd, ^{2}J(PC) = ^{3}J(PC) = 3.05Hz, **C**H$_2$CH$_2$**C**H$_2$), 27.81 (s, CH$_2$**C**H$_2$CH$_2$); ^{31}P-NMR: δ = -1.56(s). EI-MS: m/z (%): 464 (95) $[M]^+$, 422 (30) $[M\text{-}NCH_2CH_2]^+$.

43: From 0.466g (1.00 mmol) of **37** and 1.0 g (5.00mmol) $(NH_2)_2(C:O)\cdot H_2O_2$.

Yield: 0.429g (86%); m.p.: 293°C.

$C_{22}H_{16}N_2O_8P_2$ (498.32)

Analysis: C 53.67 (calcd.: 53.03), H 3.75 (3.24), N 5.22 (5.62)%.

^{1}H-NMR: δ = 3.80-4.70 (m, 4H, C**H**$_2$C**H**$_2$), 6.90-8.20 (m, 12H, **H**aromatic), ^{13}C-NMR: δ = 162.52 (d, ^{2}J(PC) = 6.81Hz, **C**(:O)NP), 150.06 (d, ^{2}J(PC) = 5.78Hz, **C**-O-P), 136.10-117.12 (m, other aromatic **C** atoms), 43.76 (dd, ^{2}J(PC) = ^{3}J(PC) = 3.01Hz, P-N**C**H$_2$); ^{31}P-NMR: δ = 1.69 (s). EI-MS: m/z (%): 498 (70) $[M]^+$, 456 (50) $[M\text{-}NC_2H_4]^+$.

44: From 0.480 g (1.00 mmol) of **38** and 1.0 g (5.00mmol) $(NH_2)_2C(:O)\cdot H_2O_2$.

Yield: 0.450g (88%); m.p.: 240°C.

$C_{23}H_{18}N_2O_8P_2$ (512.34)

Analysis: C 54.67 (calcd.: 53.92), H 3.81 (3.54), N 5.11 (5.47)%.

^{1}H-NMR: δ = 2.40 (m, 2H, $CH_2C\mathbf{H}_2CH_2$), 3.60-4.60 (m, 4H, $C\mathbf{H}_2CH_2C\mathbf{H}_2$), 6.70-8.20 (m, 12H, **H**aromatic), ^{13}C-NMR: δ = 162.40 (d, ^{2}J(PC) = 7.00Hz, **C**(:O)NP), 149.00-117.20 (m, other aromatic **C** atoms), 39.10 (d, ^{2}J(PC) = 5.05Hz, $\mathbf{C}H_2CH_2\mathbf{C}H_2$), 30.99 (s, $CH_2\mathbf{C}H_2CH_2$); ^{31}P-NMR: δ = -5.91 (s). EI-MS: m/z (%): 512 (100) $[M]^+$, 470(50) $[M\text{-}NCH_2CH_2]^+$.

45: From 0.516 g (1.00 mmol) of **39** and 1.0 g (5.00mmol) $(NH_2)_2C(:O)\cdot H_2O_2$.

Yield: 0.504g (92%); m.p.: >300°C.

$C_{26}H_{18}N_2O_8P_2$ (548.39)

Analysis: C 56.99 (calcd.: 56.95), H 3.64 (3.31), N 5.01 (5.11)%.

^{1}H-NMR: δ = 3.60-4.80 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2$), 7.00-8.20 (m, 14H, **H**aromatic), ^{13}C-NMR: δ = 162.58 (d, ^{2}J(PC) = 6.44Hz, **C**(:O)NP), 150.11 (d, ^{2}J(PC) = 6.87Hz, **C**-O-P), 140.00-117.16 (m, other aromatic **C** atoms), 43.91(dd, ^{2}J(PC) = ^{3}J(PC) = 3.00Hz, P-N$\mathbf{C}H_2$); ^{31}P-NMR: δ = -5.44 (s). EI-MS: m/z (%): 548 (50) $[M]^+$, 506(10) $[M\text{-}NC_2H_4]^+$.

46: From 0.530 g (1.00 mmol) of **40** and 1.0 g (5.00mmol) $(NH_2)_2C(:O)\cdot H_2O_2$.

Yield: 0.483g (86%); m.p.: >300°C.

$C_{27}H_{20}N_2O_8P_2$ (562.41)

Analysis: C 57.99 (calcd.: 57.66), H 3.64 (3.58), N 4.41 (4.98)%.

^{1}H-NMR: δ = 2.51 (m, 2H, $CH_2C\mathbf{H}_2CH_2$), 3.70-4.90 (m, 4H, $C\mathbf{H}_2CH_2C\mathbf{H}_2$), 7.10-8.50 (m, 14H, **H**aromatic). ^{13}C-NMR: δ = 162.53 (d, ^{2}J(PC) = 7.12Hz, **C**(:O)NP), 150.00-117.20 (m, other aromatic **C** atoms), 39.12 (d, ^{2}J(PC) = 5.08Hz, $\mathbf{C}H_2CH_2\mathbf{C}H_2$), 27.55 (s, $CH_2\mathbf{C}H_2CH_2$); ^{31}P-NMR: δ = -5.70 (s). EI-MS: m/z (%): 562 (100) $[M]^+$.

*Preparation of compounds **49-52***

The preparation of **49** is described as a typical example.

Bis(trimethylsiloxy)benzene (0.524 g, 2.06 mmol) was added to a suspension of 0.95 g (2.08 nmol) of **6** in 60 ml of dichloromethane. The mixture was stirred for 4 days (during this time the ^{31}P-NMR signal for the starting compound **6** disappeared). After removal of the solvent, the product was obtained by recrystallization from dichloromethane/diethyl ether.

49: From 0.95g (2.08mmol) of **6** and 0.52g (2.06mmol) of Bis(trimethylsiloxy)benzene

Yield: 0.608g (60%); m.p.: 168 °C.

$C_{24}H_{22}N_4O_4P_2$ (492.41)

Analysis: C 58.91 (calcd.: 58.54), H 4.95 (4.50), N 10.86 (11.38)%.

^{1}H-NMR: δ = 3.20-4.70 (m, 4H, C**H**$_2$C**H**$_2$), 3.55 (d, 6H, ^{3}J(PH)= 11.19Hz, P-N-C**H**$_3$), 6.60-8.15 (m, 12H, **H**aromatic), ^{31}P-NMR: δ = 114.44 (s). EI-MS: m/z (%): 492 (40) [M^+], 400 (100) [M^+-OC_6H_4].

50: From 0.93g (2.05) of **7** and 0.62g (2.05mmol) of Bis(trimethylsiloxy)benzene

Yield: 0.643g (62%); m.p.: 140 °C.

$C_{25}H_{24}N_4O_4P_2$ (506.44)

Analysis: C 60.01 (calcd.: 59.29), H 4.95 (4.78), N 10.86 (11.06)%.

^{1}H-NMR: δ = 2.52 (m, 2H, CH_2C**H**$_2$$CH_2$), 3.28 (d, 6H, ^{3}J(PH)= 13.91Hz, P-N-CH_3), 3.38-4.64 (m, 4H, C**H**$_2$$CH_2$C**H**$_2$), 6.70-8.40 (m, 12H, **H**aromatic), ^{13}C-NMR: δ = 163.42 (d, ^{2}J(PC)= 6.52Hz, **C**(:O)NP), 145.90 –111.12 (m, other aromatic **C** atoms), 42.85 (d, ^{2}J(PC) = 33.78Hz, **C**H_2CH_2**C**H_2), 36.56 (d, ^{2}J(PC) = 45.77Hz, PN**C**H_3), 29.16 (t, ^{3}J(PC) = 5.45Hz, CH_2**C**H_2CH_2), ^{31}P-NMR: δ = 114.98 (s). EI-MS: m/z (%): 506 (40) [M^+], 414 (100) [M^+-OC_6H_4].

51: From 0.96g (2.05mmol) of **6** and 0.51g (2.02mmol) of Bis(trimethylsiloxy)naphthalene

Yield: 0.679g (62%); m.p.: 280 °C.

$C_{28}H_{24}N_4O_4P_2$ (542.47)

Analysis: C 61.12 (calcd.: 62.00), H 4.54 (4.46), N 10.16 (10.33)%.

^{1}H-NMR: δ = 3.60-4.80 (m, 4H, C**H**$_2$C**H**$_2$), 3.14 (d, 6H, ^{3}J(PH)= 14.38Hz, P-N-C**H**$_3$), 6.90-8.20 (m, 14H, **H**aromatic), ^{31}P-NMR: δ = 117.53(s). EI-MS: m/z (%): 542 (100) [M^+], 400 (10) [M^+-$OC_{10}H_6$], 385 (30) [M^+-$OC_{10}H_6O$].

52: From 0.97g (2.07mmol) of **7** and 0.62g (2.04mmol) of Bis(trimethylsiloxy)naphthalene

Yield: 0.715g (63%); m.p.: 172 °C.

$C_{29}H_{26}N_4O_4P_2$ (556.50)

Analysis: C 62.99 (calcd.: 62.59), H 4.95 (4.71), N 9.86 (10.07)%.

^{1}H-NMR: δ = 2.52 (m, 2H, $CH_2C\mathbf{H}_2CH_2$), 3.32 (d, 6H, ^{3}J(PH)= 13.84Hz, P-N-C$\mathbf{H}_3$), 3.35-4.64 (m, 4H, $C\mathbf{H}_2CH_2C\mathbf{H}_2$), 6.70-8.40 (m, 14H, **H**aromatic), ^{13}C-NMR: δ = 163.40 (d, ^{2}J(PC)= 6.35Hz, **C**(:O)NP), 146.00 –107.00 (m, other aromatic **C** atoms), 42.80 (d, ^{2}J(PC) = 33.52Hz, $\mathbf{C}H_2CH_2\mathbf{C}H_2$), 36.80(d, ^{2}J(PC) = 45.64Hz, PN**C**H_3), 29.31 (t, ^{3}J(PC) = 5.30Hz, $CH_2\mathbf{C}H_2CH_2$), ^{31}P-NMR: δ = 114.14 (s). EI-MS: m/z (%): 556 (30) [M^+], 414 (60) [M^+-$OC_{10}H_6$].

*Preparation of compounds **55-58***

The preparation of **55** is described as a typical example.

To a solution of 0.492 g (1.00 mmole) of **47** in 60 ml dichloromethane was added 1.0 g (0.02mol,excess) of $(NH_2)_2(C{:}O)\cdot H_2O_2$ at room temperature. The reaction mixture was stirred for 24 hours and was then filtered. The filtrate was washed with 2x10ml of water and was then dried over $MgSO_4$ overnight. After filtration and removal of the solvent the product was obtained as a white solid.

55: From 0.492 g (1.00 mmol) of **49** and 1.0g (0.02mol,excess) of $(NH_2)_2(C{:}O)\cdot H_2O_2$

Yield: 0.446g (85%); m.p.: 200 °C.

$C_{25}H_{24}N_4O_6P_2$ (524.44)

Analysis: C 55.97 (calcd.: 55.77), H 4.75 (4.49), N 10.22 (10.41)%.

^{1}H-NMR: δ = 3.30 (d, 6H, ^{3}J(PH)= 7.80 Hz, P-N-C$\mathbf{H}_3$), 3.40-4.50 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2$), 6.80-8.20 (m, 12H, **H**aromatic), ^{13}C-NMR: δ = 163.80 (d, ^{2}J(PC)= 5.00 Hz, **C**(:O)NP), 142.50 – 114.80 (m, other aromatic **C** atoms), 39.10 (d, ^{2}J(PC) = 5.50Hz, $\mathbf{C}H_2\mathbf{C}H_2$), 31.84 (d, ^{2}J(PC) = 5.20 Hz, PN**C**H_3), ^{31}P-NMR: δ = 3.00 (s). EI-MS: m/z (%): 524 (80) [M^+], 422(10) [M^+-OC_6H_4].

56: From 0.50 g (1.00 mmol) of **50** and 1.0g (0.02mol, excess) of $(NH_2)_2(C{:}O)\cdot H_2O_2$

Yield: 0.495 g (92%), m.p.: 200 °C.

$C_{25}H_{24}N_4O_6P_2$ (538.44)

Analysis: C 55.97 (calcd.: 55.77), H 4.75 (4.49), N 10.22 (10.41)%.

^{1}H-NMR: δ = 2.51 (m, 2H, $CH_2C\mathbf{H}_2CH_2$), 3.32 (d, 6H, ^{3}J(PH)= 7.79 Hz, P-N-CH_3), 3.38-4.50 (m, 4H, $C\mathbf{H}_2CH_2C\mathbf{H}_2$), 6.88-8.20 (m, 12H, **H**aromatic), ^{13}C-NMR: δ = 163.82 (d, ^{2}J(PC)= 5.23 Hz, **C**(:O)NP), 142.50 –114.80 (m, other aromatic **C** atoms), 39.10 (d, ^{2}J(PC) = 5.65Hz, $\mathbf{C}H_2CH_2\mathbf{C}H_2$), 31.84 (d, ^{2}J(PC) = 4.22Hz, PN**C**H_3), 27.94 (s, $CH_2\mathbf{C}H_2CH_2$), ^{31}P-NMR: δ = 2.81(s). EI-MS: m/z (%): 538 (100) [M^+], 446 (10) [M^+-OC_6H_4].

57: Starting from 0.54 g (1.00 mmole) of **50** and 1.0g (0.02mol, excess) of $(NH_2)_2(C{:}O)\cdot H_2O_2$

Yield: 0.510 g (89%), m.p.: 340 °C.

$C_{28}H_{24}N_4O_6P_2$ (574.46)

Analysis: C 58.15 (calcd.: 58.54), H 4.35 (4.21), N 9.60 (9.75)%.

^{1}H-NMR: δ = 4.00-4.70 (m, 4H, $C\mathbf{H}_2C\mathbf{H}_2$), 3.33 (d, 6H, ^{3}J(PH)= 8.84Hz, P-N-$C\mathbf{H}_3$), 7.00-8.20 (m, 14H, **H**aromatic), ^{13}C-NMR: δ = 163.71 (d, ^{2}J(PC)= 4.28Hz, **C**(:O)NP), 141.60-114.30 (m, other aromatic **C** atoms), 43.66 (d, ^{2}J(PC) = 4.01Hz, P-N**C**H_2), 31.40 (d, ^{2}J(PC) = 5.20Hz, P-N**C**H_3); ^{31}P-NMR: δ = 4.61 (s). EI-MS: m/z (%): 574 (95) [M^+], 558 (10) [M^+-O].

58: Starting from 0.56 g (1.00 mmole) of **51** and 1.0g (0.02mol,excess) of

$(NH_2)_2(C{:}O)\cdot H_2O_2$

Yield: 0.535g (91%), m.p.: 339 °C.

$C_{29}H_{26}N_4O_6P_2$ (588.50)

Analysis: C 59.97 (calcd.: 59.19), H 4.70 (4.45), N 9.34 (9.52)%.

^{1}H-NMR: δ = 2.55 (m, 2H, $CH_2C\mathbf{H}_2CH_2$), 3.38 (d, 6H, ^{3}J(PH)= 8.72Hz, P-N-$C\mathbf{H}_3$), 3.50-4.60 (m, 4H, $C\mathbf{H}_2CH_2C\mathbf{H}_2$), 6.80-8.60 (m, 14H, **H**aromatic), ^{13}C-NMR: δ = 163.50 (d, ^{2}J(PC)= 4.00 Hz, **C**(:O)NP), 145.00 –114.00 (m, other aromatic **C** atoms), 39.15 (d, ^{2}J(PC) = 5.60Hz, $\mathbf{C}H_2CH_2\mathbf{C}H_2$), 32.05 (d, ^{2}J(PC) = 4.16Hz, PN**C**H_3), 28.07 (s, $CH_2\mathbf{C}H_2CH_2$), ^{31}P-NMR: δ = 3.14 (s). EI-MS: m/z (%): 588 (100) [M^+], 572 (10) [M^+-O].

*Preparation of compounds **61** and **62:***

The preparation of **61** is described as a typical example.

A mixture of 0.542 g (1.00 mmole) of **51** and 0.064g (2.00 mmol) of elemental sulfur in 40ml of toluene was heated under reflux for 2 days (during this time the ^{31}P-NMR signal for the starting compound **51** disappeared). After filtration and removal of the solvent the product was obtained and was purified by crystallization from dichloromethane and diethyl ether.

61: Yield: 0.43g (71%), m.p.: >300 °C.

$C_{28}H_{24}N_4O_4P_2S_2$ (606.60)

Analysis: C 56.97 (calcd.: 55.44), H 4.70 (3.99), N 8.84 (9.24), S 10.55 (12.01)%.

^{1}H-NMR: δ = 4.40-5.00 (m, 4H, C**H**$_2$C**H**$_2$), 3.50 (d, 6H, ^{3}J(PH)= 12.20Hz, P-N-C**H**$_3$), 6.60-8.30 (m, 14H, **H**aromatic); ^{31}P-NMR: δ = 66.62(s). EI-MS: m/z (%): 606 (100) [M^+], 574 (5) [M^+-S], 542 (5) [M^+-2xS].

62: This compound was obtained from 0.56 g (1.00 mmol) of **52** and 0.06 g (2.00mmol) of elemental sulfur in 40 ml of toluene as described for **61**.

Yield: 0.42g (68%), m.p.: 175 °C.

$C_{29}H_{26}N_4O_4P_2S_2$ (620.63)

Analysis: C 56.97 (calcd.: 56.12), H 4.70 (4.22), N 8.84 (9.03), S 10.31 (11.87)%.

^{1}H-NMR: δ = 2.70 (m, 2H, CH$_2$C**H**$_2$CH$_2$), 3.30 (d, 6H, ^{3}J(PH)= 7.06Hz, P-N-C**H**$_3$), 3.50-4.60 (m, 4H, C**H**$_2$CH$_2$C**H**$_2$), 6.80-8.60 (m, 14H, **H**aromatic), ^{31}P-NMR: δ = 73.28(s). EI-MS: m/z (%): 620 (20) [M^+].

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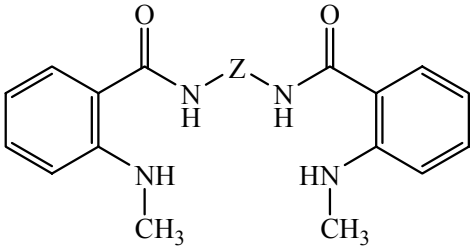
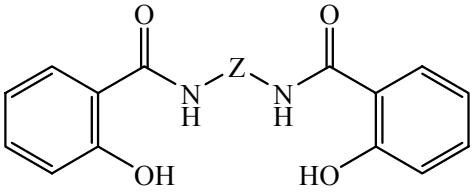
9. List of the Numbered Compounds:

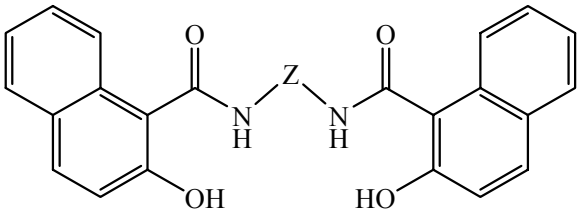
***= known compounds**



1: Z = CH_2CH_2 *
2: Z = $CH_2CH_2CH_2$ *



3: Z = CH_2CH_2 *
4: Z = $CH_2CH_2CH_2$ *



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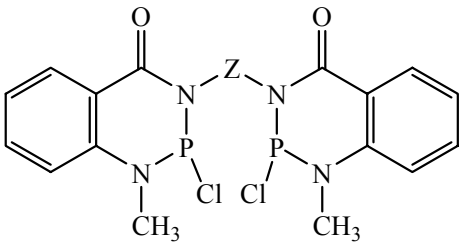
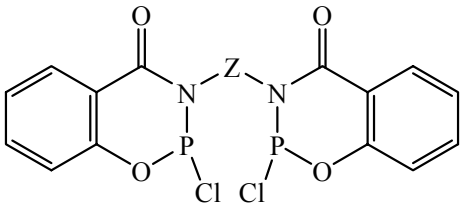


6: Z = CH_2CH_2 *
7: Z = $CH_2CH_2CH_2$ *



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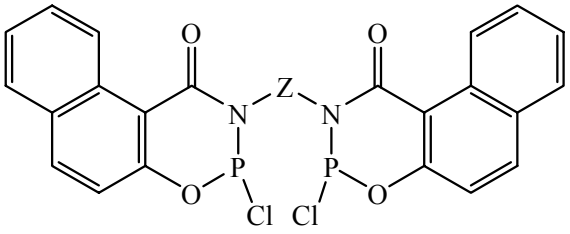
9: Z = $CH_2CH_2CH_2$



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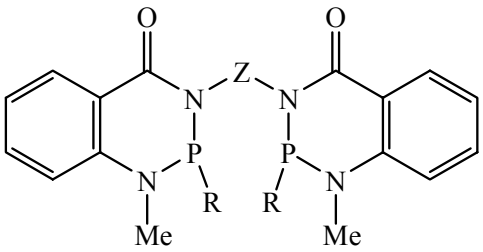
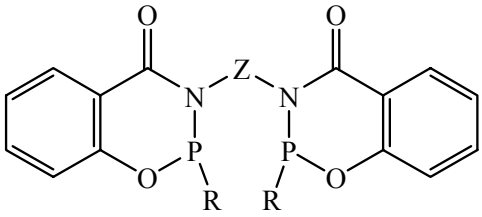


11: R = NMe_2, Z = CH_2CH_2
12: R = $N(CH_2CH_2)_2O$,
Z = CH_2CH_2



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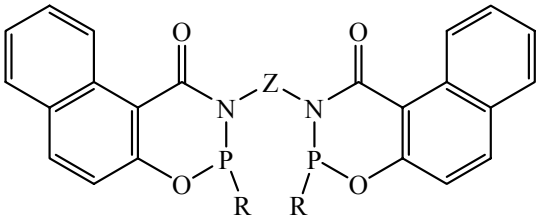
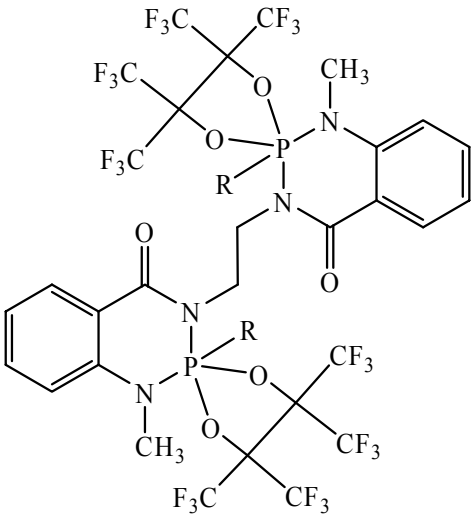
Z = CH_2CH_2



14: R = NMe_2, Z = CH_2CH_2
15: R = NEt_2, Z = CH_2CH_2
16: R = $N(CH_2CH_2)_2O$, Z = CH_2CH_2
17: R = NHPh, Z = CH_2CH_2



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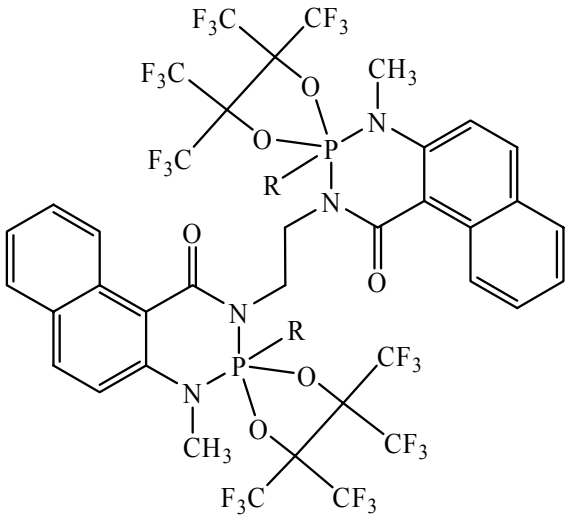
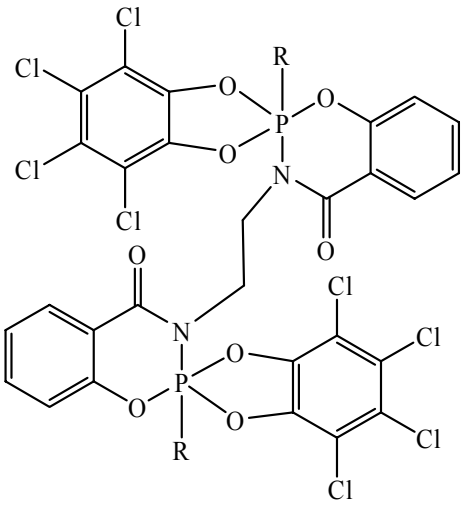


19: R = $N(CH_3)_2$
20: R = $N(CH_2CH_3)_2$
21: R = $N(CH_2CH_2)_2O$
22: R = NHPh

.



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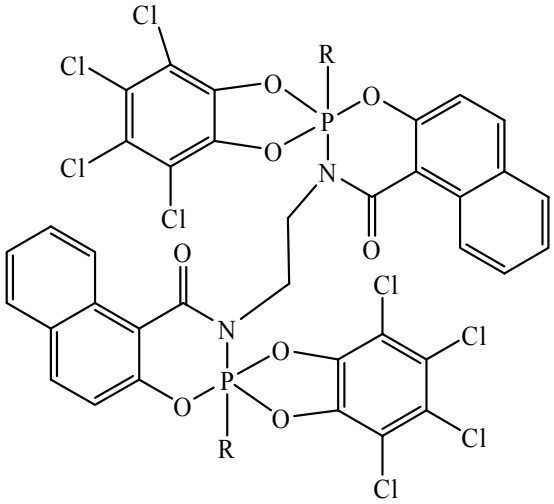
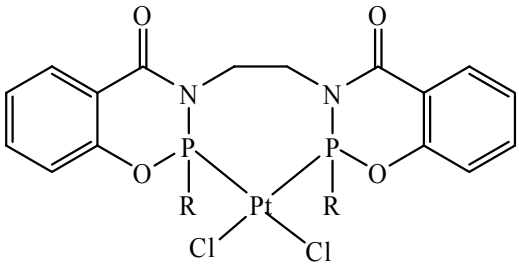


24: R = $N(CH_3)_3$
25: R = $N(CH_2CH_2)_2O$



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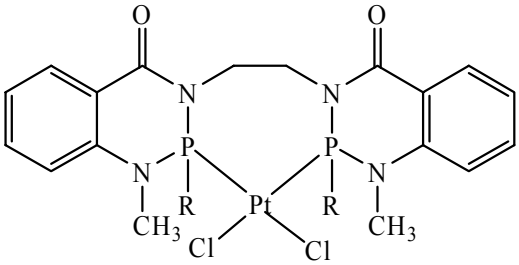

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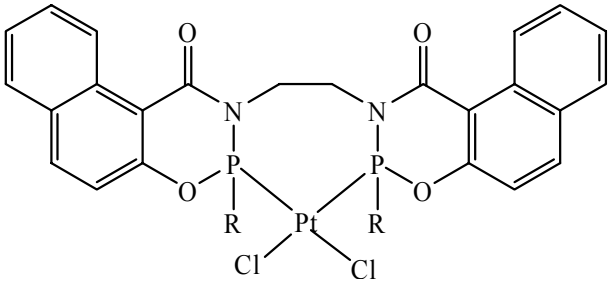
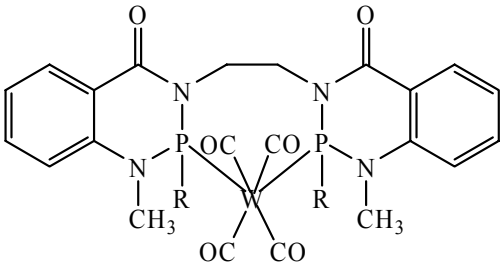


28: R = $N(CH_3)_2$
29: R = $N(CH_2CH_3)_2$
30: R = $N(CH_2CH_2)_2O$
31: R = NHPh



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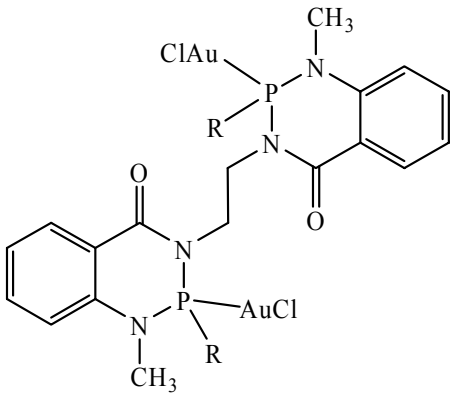

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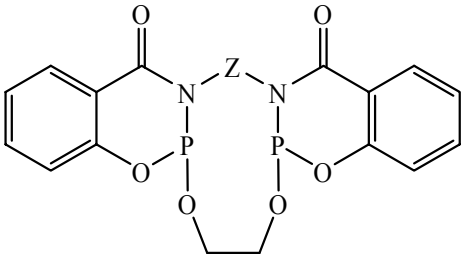

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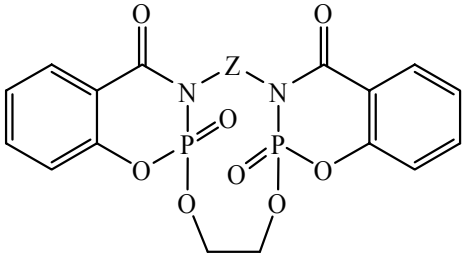
36: Z = $CH_2CH_2CH_2$



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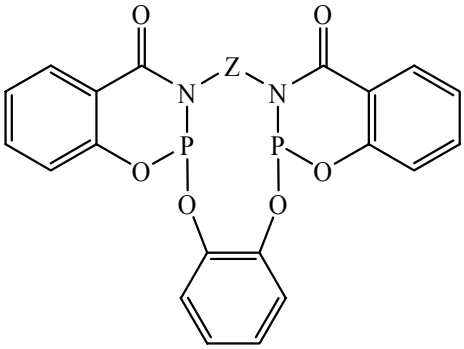

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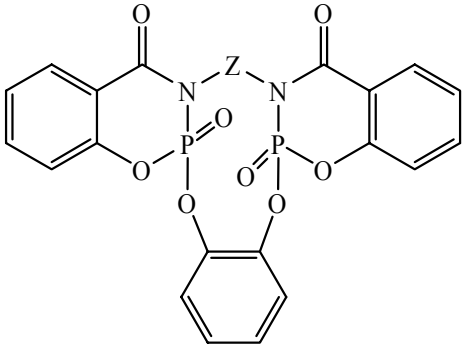
38: Z = $CH_2CH_2CH_2$



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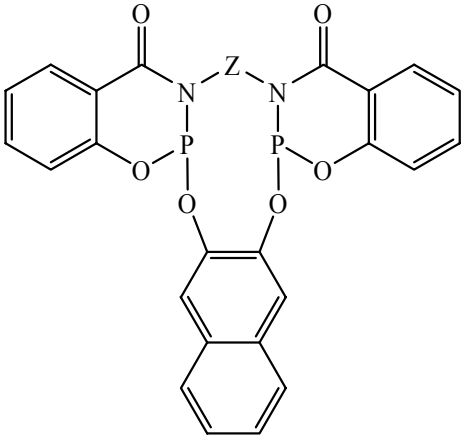
44: Z = $CH_2CH_2CH_2$



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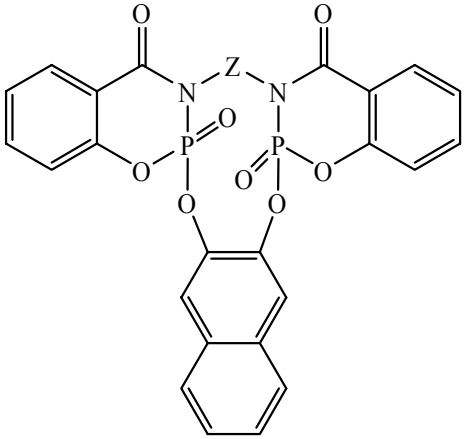

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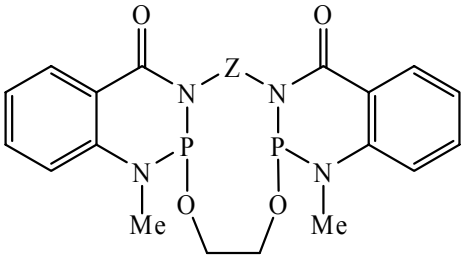
46: Z = $CH_2CH_2CH_2$



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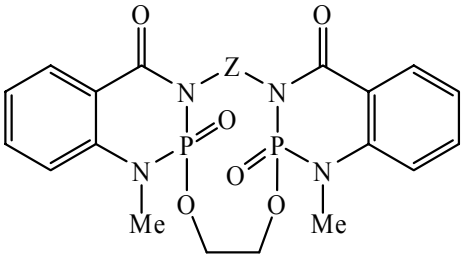
48: Z = $CH_2CH_2CH_2$



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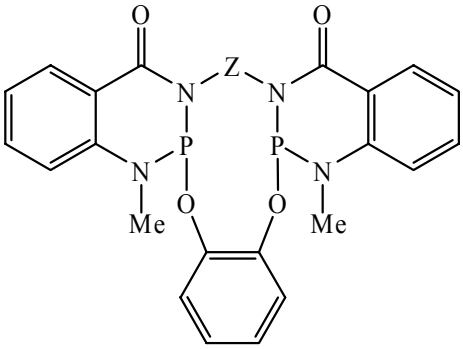
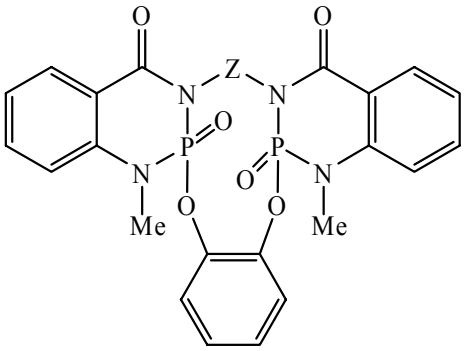
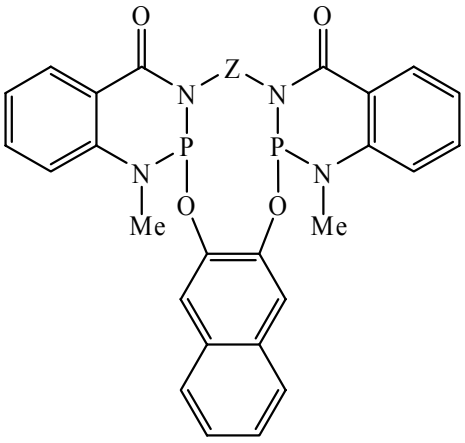
54: Z = $CH_2CH_2CH_2$



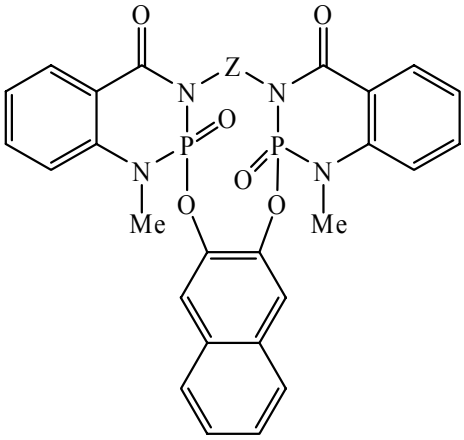
49: Z = CH_2CH_2
50: Z = $CH_2CH_2CH_2$



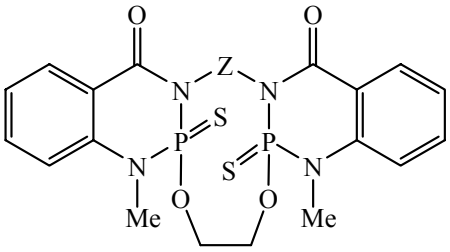
55: Z = CH_2CH_2
56: Z = $CH_2CH_2CH_2$



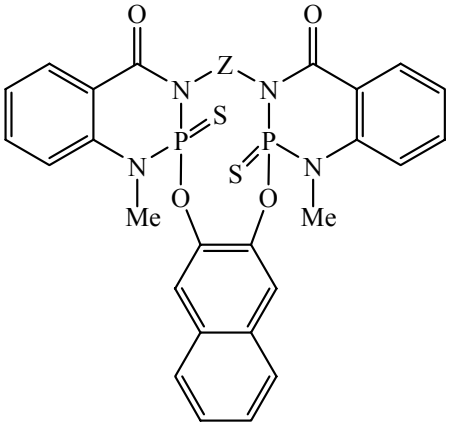
51: Z = CH_2CH_2
52: Z = $CH_2CH_2CH_2$



57: Z = CH_2CH_2
58: Z = $CH_2CH_2CH_2$



59: Z = CH_2CH_2
60: Z = $CH_2CH_2CH_2$



61: Z = CH_2CH_2
62: Z = $CH_2CH_2CH_2$

10. Appendix

List of Abbreviations

XX	Number of compound	s	singlet
(XX)	Number of equation	d	dublet
[XX]	Reference XX	t	triplet
b.p.	boiling point	dd	dublet of dublets
calcd.	calculated		
EI	Electron Impact	$^{n}J(AB)$	coupling constant of nuclei A and B over n bonds
Eqn.	Equation	$[M]^{+}$	molecular ion
FAB	Fast Atom Bombardment	Hz	Hertz
Fig.	Figure	pm	picometer (10^{-12} m)
h	hours	ppm	parts per million
HFA	hexafluoroacetone		
min	minute(s)	δ	chemical shift (ppm)
m.p.	melting point	$\sigma^{x}P$	phosphorus atom with number coordination x
MS	Mass spectrometry	$\lambda^{x}P$	phosphorus atom with oxidation number x
TMS	tetramethylsilane	ν	wave number (cm^{-1})
TOB	Tetrachloroorthobenzoquinone		
Me	Methyl		
Et	Ethyl		
Ph	Phenyl		

11. X-ray data for compounds

Table 1. Crystal data and structure refinement for **19**.

Identification code	luft	
Empirical formula	$C_{41}\ H_{30}\ Cl_2\ F_{24}\ N_4\ O_8\ P_2$	
Formula weight	1295.53	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 912.54(16) pm	α= 104.359(6)°
	b = 1028.50(18) pm	β= 94.110(6)°
	c = 1402.2(2) pm	γ = 109.093(6)°
Volume, Z	1.1879(4) nm^3, 1	
Density (calculated)	1.811 Mg/m^3	
Absorption coefficient	0.357 mm^{-1}	
F(000)	648	
Crystal size	0.21 x 0.19 x 0.06 mm	
Theta range for data collection	1.52 to 25.02°	
Index ranges	$-10 \le h \le 10, -12 \le k \le 12, -16 \le l \le 16$	
Reflections collected	12297	
Independent reflections	4187 [$R_{Int.}$= 0.0970]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Data / restraints / parameters	4187 / 21 / 380	
Goodness-of-fit on F^2	0.990	
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.1296	
R indices (all data)	R1 = 0.0909, wR2 = 0.1474	
Largest diff. peak and hole	597 and-964 e nm^{-3}	

Table 2. Bond lengths [Å] and angles [°] for **19**.

P-N(2)	162.1(3)	C(8)-C(9)	141.2(5)
P-O(1)	165.1(3)	C(9)-C(10)	144.8(5)
P-O(3)	166.4(3)	C(10)-C(11)	147.7(5)
P-N(1)	170.2(3)	C(12)-C(12)#1	153.9(6)
P-O(4)	172.8(3)	C(15)-C(16)	157.4(5)
O(1)-C(1)	138.0(4)	C(15)-C(18)	160.0(6)
O(2)-C(11)	121.8(4)	C(18)-C(20)	155.8(5)
O(3)-C(15)	139.8(4)	C(18)-C(19)	157.8(5)
O(4)-C(18)	139.3(4)	Cl-C(99)#2	151.7(11)
N(1)-C(11)	139.6(4)	Cl-C(99)#3	160.9(11)
N(1)-C(12)	147.4(4)	C(99)-C(99)#4	128(2)
N(2)-C(13)	147.1(5)	C(99)-Cl#2	151.7(11)
N(2)-C(14)	148.4(5)	C(99)-Cl#5	160.9(11)
F(1)-C(16)	132.1(5)		
F(2)-C(16)	133.8(5)	N(2)-P-O(1)	93.33(14)
F(3)-C(16)	132.9(4)	N(2)-P-O(3)	126.42(14)
C(17)-F(5')	129.2(13)	O(1)-P-O(3)	84.56(13)
C(17)-F(6')	131.2(14)	N(2)-P-N(1)	114.40(15)
C(17)-F(6)	131.4(5)	O(1)-P-N(1)	92.80(13)
C(17)-F(4)	131.9(5)	O(3)-P-N(1)	119.18(13)
C(17)-F(5)	132.8(5)	N(2)-P-O(4)	92.42(14)
C(17)-F(4')	133.1(12)	O(1)-P-O(4)	170.71(12)
C(17)-C(15)	156.6(5)	O(3)-P-O(4)	86.15(12)
F(7)-C(19)	131.4(4)	N(1)-P-O(4)	91.47(13)
F(8)-C(19)	133.0(4)	C(1)-O(1)-P	118.6(2)
F(9)-C(19)	132.8(5)	C(15)-O(3)-P	120.9(2)
F(10)-C(20)	133.0(5)	C(18)-O(4)-P	117.2(2)
F(11)-C(20)	132.6(5)	C(11)-N(1)-C(12)	115.6(3)
F(12)-C(20)	132.8(4)	C(11)-N(1)-P	125.3(2)
C(1)-C(10)	138.0(5)	C(12)-N(1)-P	119.1(2)
C(1)-C(2)	140.3(5)	C(13)-N(2)-C(14)	109.3(3)
C(2)-C(3)	135.8(5)	C(13)-N(2)-P	127.7(3)
C(3)-C(4)	142.8(5)	C(14)-N(2)-P	122.4(3)
C(4)-C(5)	141.2(5)	F(5')-C(17)-F(6')	110.1(17)
C(4)-C(9)	142.6(5)	F(5')-C(17)-F(6)	123.8(13)
C(5)-C(6)	135.7(5)	F(6')-C(17)-F(6)	22.8(14)
C(6)-C(7)	139.0(6)	F(5')-C(17)-F(4)	82.4(12)
C(7)-C(8)	137.3(5)	F(6')-C(17)-F(4)	127.2(15)

F(6)-C(17)-F(4)	107.8(4)	N(1)-C(11)-C(10)	116.3(3)
F(5')-C(17)-F(5)	27.0(12)	N(1)-C(12)-C(12)#1	109.8(4)
F(6')-C(17)-F(5)	87.0(14)	O(3)-C(15)-C(17)	108.6(3)
F(6)-C(17)-F(5)	105.7(4)	O(3)-C(15)-C(16)	104.8(3)
F(4)-C(17)-F(5)	107.8(4)	C(17)-C(15)-C(16)	108.1(3)
F(5')-C(17)-F(4')	114.3(13)	O(3)-C(15)-C(18)	102.3(3)
F(6')-C(17)-F(4')	103.5(14)	C(17)-C(15)-C(18)	117.6(3)
F(6)-C(17)-F(4')	80.9(12)	C(16)-C(15)-C(18)	114.4(3)
F(4)-C(17)-F(4')	33.6(12)	F(1)-C(16)-F(3)	107.1(3)
F(5)-C(17)-F(4')	136.1(12)	F(1)-C(16)-F(2)	108.5(3)
F(5')-C(17)-C(15)	114.1(12)	F(3)-C(16)-F(2)	108.7(3)
F(6')-C(17)-C(15)	109.3(16)	F(1)-C(16)-C(15)	110.4(3)
F(6)-C(17)-C(15)	112.6(4)	F(3)-C(16)-C(15)	111.0(3)
F(4)-C(17)-C(15)	111.1(4)	F(2)-C(16)-C(15)	111.0(3)
F(5)-C(17)-C(15)	111.6(3)	O(4)-C(18)-C(20)	108.0(3)
F(4')-C(17)-C(15)	104.9(10)	O(4)-C(18)-C(19)	108.7(3)
C(10)-C(1)-O(1)	120.7(3)	C(20)-C(18)-C(19)	106.1(3)
C(10)-C(1)-C(2)	123.2(3)	O(4)-C(18)-C(15)	102.0(3)
O(1)-C(1)-C(2)	116.2(3)	C(20)-C(18)-C(15)	117.3(3)
C(3)-C(2)-C(1)	119.2(4)	C(19)-C(18)-C(15)	114.3(3)
C(2)-C(3)-C(4)	121.2(4)	F(7)-C(19)-F(9)	107.6(3)
C(5)-C(4)-C(9)	119.6(3)	F(7)-C(19)-F(8)	107.8(3)
C(5)-C(4)-C(3)	120.6(3)	F(9)-C(19)-F(8)	106.3(3)
C(9)-C(4)-C(3)	119.7(3)	F(7)-C(19)-C(18)	113.0(3)
C(6)-C(5)-C(4)	120.7(4)	F(9)-C(19)-C(18)	109.7(3)
C(5)-C(6)-C(7)	120.2(4)	F(8)-C(19)-C(18)	112.1(3)
C(8)-C(7)-C(6)	121.0(4)	F(11)-C(20)-F(12)	108.3(3)
C(7)-C(8)-C(9)	120.7(4)	F(11)-C(20)-F(10)	107.0(3)
C(8)-C(9)-C(4)	117.7(3)	F(12)-C(20)-F(10)	108.0(3)
C(8)-C(9)-C(10)	124.0(3)	F(11)-C(20)-C(18)	111.7(3)
C(4)-C(9)-C(10)	118.3(3)	F(12)-C(20)-C(18)	111.5(3)
C(1)-C(10)-C(9)	118.4(3)	F(10)-C(20)-C(18)	110.2(3)
C(1)-C(10)-C(11)	118.8(3)	C(99)#2-Cl-C(99)#3	48.1(7)
C(9)-C(10)-C(11)	122.6(3)	C(99)#4-C(99)-Cl#2	69.7(9)
O(2)-C(11)-N(1)	119.2(3)	C(99)#4-C(99)-Cl#5	62.2(8)
O(2)-C(11)-C(10)	124.5(3)	Cl#2-C(99)-Cl#5	131.9(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 -x,-y+1,-z+1 #3 x,y-1,z

#4 -x,-y+2,-z+1 #5 x,y+1,z

Table 3. Crystal data and structure refinement for **28**.

Identification code	lupi	
Empirical formula	$C_{28}H_{28}Cl_2N_4O_4P_2Pt$	
Formula weight	812.47	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 1310.30(8) pm	α= 90°
	b = 1300.79(8) pm	β= 110.955(3)°
	c = 1810.71(10) pm	γ = 90°
Volume Z	2.8821(3) nm^3, 4	
Density (calculated)	1.872 Mg/m^3	
Absorption coefficient	5.208 mm^{-1}	
F(000)	1592	
Crystal size	0.30 x 0.20 x 0.14 mm	
Theta range for data collection	1.67 to 30.52°	
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 18$, $-25 \le l \le 25$	
Reflections collected	53360	
Independent reflections	8785 [$R_{Int.}$ = 0.0257]	
Completeness to theta = 25.03°	99.8 %	
Absorption correction	Multiple scans (SADABS)	
Max. and min. Transmission	0.8945 and 0.6236	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Data / restraints / parameters	8785 / 85 / 374	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0158, wR2 = 0.0387	
R indices (all data)	R1 = 0.0196, wR2 = 0.0396	
Largest diff. peak and hole	1124 and -366 e nm^{-3}	

Table 4. Bond lengths [Å] and angles [°] for **28**.

Pt-P'	220.42(4)	C(3')-C(4')	141.5(2)
Pt-P	221.44(4)	C(4')-C(5')	141.7(3)
Pt-Cl	235.10(4)	C(4')-C(9')	142.9(2)
Pt-Cl'	235.96(4)	C(5')-C(6')	137.3(3)
P-O(1)	160.97(12)	C(6')-C(7')	139.6(3)
P-N(2)	161.79(15)	C(7')-C(8')	137.9(3)
P-N(1)	169.54(14)	C(8')-C(9')	142.5(2)
O(1)-C(1)	139.3(2)	C(9')-C(10')	144.2(2)
O(2)-C(11)	121.3(2)	C(10')-C(11')	149.2(2)
N(1)-C(11)	140.4(2)		
N(1)-C(12)	148.03(19)	P'-Pt-P	98.298(15)
N(2)-C(13)	146.4(2)	P'-Pt-Cl	174.335(15)
N(2)-C(14)	146.7(2)	P-Pt-Cl	87.281(16)
C(1)-C(10)	137.2(2)	P'-Pt-Cl'	84.806(15)
C(1)-C(2)	140.5(2)	P-Pt-Cl'	176.612(14)
C(2)-C(3)	135.3(3)	Cl-Pt-Cl'	89.594(15)
C(3)-C(4)	142.3(3)	O(1)-P-N(2)	105.49(7)
C(4)-C(5)	141.3(3)	O(1)-P-N(1)	97.57(6)
C(4)-C(9)	143.0(2)	N(2)-P-N(1)	104.19(7)
C(5)-C(6)	136.4(3)	O(1)-P-Pt	111.09(4)
C(6)-C(7)	140.2(3)	N(2)-P-Pt	115.59(6)
C(7)-C(8)	137.5(3)	N(1)-P-Pt	120.60(5)
C(8)-C(9)	142.0(3)	C(1)-O(1)-P	115.52(10)
C(9)-C(10)	144.3(2)	C(11)-N(1)-C(12)	117.10(13)
C(10)-C(11)	148.9(2)	C(11)-N(1)-P	122.63(11)
C(12)-C(12')	153.3(2)	C(12)-N(1)-P	119.59(11)
P'-O(1')	159.91(13)	C(13)-N(2)-C(14)	114.13(14)
P'-N(2')	161.79(14)	C(13)-N(2)-P	123.73(12)
P'-N(1')	168.62(13)	C(14)-N(2)-P	121.07(12)
O(1')-C(1')	138.8(2)	C(10)-C(1)-O(1)	120.04(14)
O(2')-C(11')	121.53(18)	C(10)-C(1)-C(2)	123.62(16)
N(1')-C(11')	140.0(2)	O(1)-C(1)-C(2)	116.30(15)
N(1')-C(12')	147.4(2)	C(3)-C(2)-C(1)	118.45(17)
N(2')-C(13')	145.7(2)	C(2)-C(3)-C(4)	121.79(16)
N(2')-C(14')	146.8(2)	C(5)-C(4)-C(3)	120.88(17)
C(1')-C(10')	138.1(2)	C(5)-C(4)-C(9)	119.59(18)
C(1')-C(2')	140.0(2)	C(3)-C(4)-C(9)	119.51(17)
C(2')-C(3')	136.1(3)	C(6)-C(5)-C(4)	120.99(19)

C(5)-C(6)-C(7)	119.90(19)	C(13')-N(2')-P'	124.98(12)
C(8)-C(7)-C(6)	120.9(2)	C(14')-N(2')-P'	119.33(12)
C(7)-C(8)-C(9)	120.82(19)	C(10')-C(1')-O(1')	122.14(14)
C(8)-C(9)-C(4)	117.73(17)	C(10')-C(1')-C(2')	123.49(16)
C(8)-C(9)-C(10)	124.22(16)	O(1')-C(1')-C(2')	114.34(13)
C(4)-C(9)-C(10)	118.03(16)	C(3')-C(2')-C(1')	119.10(15)
C(1)-C(10)-C(9)	118.57(15)	C(2')-C(3')-C(4')	120.97(15)
C(1)-C(10)-C(11)	119.51(15)	C(3')-C(4')-C(5')	119.85(16)
C(9)-C(10)-C(11)	121.92(15)	C(3')-C(4')-C(9')	119.89(16)
O(2)-C(11)-N(1)	120.31(15)	C(5')-C(4')-C(9')	120.21(16)
O(2)-C(11)-C(10)	123.40(16)	C(6')-C(5')-C(4')	120.69(17)
N(1)-C(11)-C(10)	116.29(14)	C(5')-C(6')-C(7')	119.42(17)
N(1)-C(12)-C(12')	111.81(12)	C(8')-C(7')-C(6')	121.86(17)
O(1')-P'-N(2')	104.39(7)	C(7')-C(8')-C(9')	120.37(17)
O(1')-P'-N(1')	99.47(6)	C(8')-C(9')-C(4')	117.43(15)
N(2')-P'-N(1')	106.31(7)	C(8')-C(9')-C(10')	124.02(15)
O(1')-P'-Pt	112.44(5)	C(4')-C(9')-C(10')	118.54(14)
N(2')-P'-Pt	113.29(5)	C(1')-C(10')-C(9')	117.78(14)
N(1')-P'-Pt	119.16(5)	C(1')-C(10')-C(11')	119.69(14)
C(1')-O(1')-P'	125.79(10)	C(9')-C(10')-C(11')	122.47(14)
C(11')-N(1')-C(12')	117.07(12)	N(1')-C(12')-C(12)	112.21(13)
C(11')-N(1')-P'	128.66(11)	O(2')-C(11')-N(1')	118.65(15)
C(12')-N(1')-P'	114.24(11)	O(2')-C(11')-C(10')	124.66(15)
C(13')-N(2')-C(14')	115.44(14)	N(1')-C(11')-C(10')	116.60(13)

Table 5. Crystal data and structure refinement for **30**.

Identification code	lustig	
Empirical formula	$C_{33} H_{33.35} Cl_{4.65} N_4 O_6 P_2 Pt$	
Formula weight	1003.77	
Temperature	293(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 1018.65(8) pm	α= 90°
	b = 2482.93(16) pm	β= 109.421(3)°
	c = 1507.94(10) pm	γ = 90°
Volume, Z	3.5969(4) nm^3, 4	
Density (calculated)	1.854 Mg/m^3	
Absorption coefficient	4.386 mm^{-1}	
F(000)	1977	
Crystal size	0.27 x 0.24 x 0.12 mm	
Theta range for data collection	1.64 to 30.51°	
Index ranges	$-14 \le h \le 14, -35 \le k \le 35, -21 \le l \le 21$	
Reflections collected	58927	
Independent reflections	10974 [$R_{Int.}$= 0.0339]	
Completeness to theta = 30.00°	99.8 %	
Absorption correction	Multiple scans (SADABS)	
Max. and min. Transmission	0.8945 and 0.6770	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Data / restraints / parameters	10974 / 450 / 478	
Goodness-of-fit on F^2	0.971	
Final R indices [I>2sigma(I)]	R1 = 0.0198, wR2 = 0.0426	
R indices (all data)	R1 = 0.0288, wR2 = 0.0445	
Largest diff. peak and hole	1047 and-526 e nm^{-3}	

Table 6. Bond lengths [Å] and angles [°] for **30**.

Pt-P(2)	221.35(5)	O(2')-C(11')	121.4(3)
Pt-P(1)	221.77(5)	O(3')-C(14')	141.9(2)
Pt-Cl(2)	233.87(5)	O(3')-C(15')	143.3(2)
Pt-Cl(1)	234.54(5)	C(1')-C(10')	137.8(3)
P(1)-O(1')	161.75(15)	C(1')-C(2')	139.8(3)
P(1)-N(2')	162.27(16)	C(2')-C(3')	136.0(3)
P(1)-N(1')	168.82(17)	C(3')-C(4')	141.3(3)
P(2)-O(1)	160.65(13)	C(4')-C(9')	142.4(3)
P(2)-N(2)	162.95(17)	C(4')-C(5')	142.9(3)
P(2)-N(1)	168.40(17)	C(5')-C(6')	135.9(3)
N(1)-C(11)	140.6(3)	C(6')-C(7')	140.3(3)
N(1)-C(12)	147.1(2)	C(7')-C(8')	137.7(3)
N(2)-C(13)	147.0(3)	C(8')-C(9')	141.7(3)
N(2)-C(16)	147.0(3)	C(9')-C(10')	144.6(3)
O(1)-C(1)	138.5(2)	C(10')-C(11')	149.6(3)
O(2)-C(11)	121.7(3)	C(13')-C(14')	151.4(3)
O(3)-C(14)	142.7(3)	C(15')-C(16')	151.2(3)
O(3)-C(15)	142.8(3)	C(99)-Cl(4)	174.4(3)
C(1)-C(10)	137.6(3)	C(99)-Cl(5)	175.1(3)
C(1)-C(2)	140.8(2)	C(99)-Cl(3)	175.8(3)
C(2)-C(3)	135.7(3)	C(99')-Cl(4')	176.4(8)
C(3)-C(4)	142.0(3)	C(99')-Cl(3')	176.5(7)
C(4)-C(5)	141.9(3)		
C(4)-C(9)	142.2(3)	P(2)-Pt-P(1)	98.164(19)
C(5)-C(6)	136.5(3)	P(2)-Pt-Cl(2)	85.539(18)
C(6)-C(7)	139.9(3)	P(1)-Pt-Cl(2)	176.121(19)
C(7)-C(8)	136.3(3)	P(2)-Pt-Cl(1)	170.280(17)
C(8)-C(9)	142.3(3)	P(1)-Pt-Cl(1)	88.163(19)
C(9)-C(10)	144.7(3)	Cl(2)-Pt-Cl(1)	88.316(18)
C(10)-C(11)	147.6(3)	O(1')-P(1)-N(2')	105.39(8)
C(12)-C(12')	152.0(3)	O(1')-P(1)-N(1')	97.68(8)
C(13)-C(14)	151.2(3)	N(2')-P(1)-N(1')	104.40(8)
C(15)-C(16)	151.9(3)	O(1')-P(1)-Pt	113.23(6)
N(1')-C(11')	140.1(2)	N(2')-P(1)-Pt	115.64(6)
N(1')-C(12')	147.5(3)	N(1')-P(1)-Pt	118.31(6)
N(2')-C(16')	147.6(2)	O(1)-P(2)-N(2)	106.28(8)
N(2')-C(13')	148.1(2)	O(1)-P(2)-N(1)	99.52(8)
O(1')-C(1')	139.8(2)	N(2)-P(2)-N(1)	103.98(9)

O(1)-P(2)-Pt	109.33(6)	C(11')-N(1')-P(1)	119.39(14)
N(2)-P(2)-Pt	116.32(7)	C(12')-N(1')-P(1)	120.57(13)
N(1)-P(2)-Pt	119.48(7)	C(16')-N(2')-C(13')	112.50(15)
C(11)-N(1)-C(12)	115.76(16)	C(16')-N(2')-P(1)	123.09(12)
C(11)-N(1)-P(2)	128.68(13)	C(13')-N(2')-P(1)	121.67(13)
C(12)-N(1)-P(2)	115.42(13)	C(1')-O(1')-P(1)	114.31(12)
C(13)-N(2)-C(16)	112.89(16)	C(14')-O(3')-C(15')	110.38(15)
C(13)-N(2)-P(2)	126.33(14)	C(10')-C(1')-O(1')	120.11(18)
C(16)-N(2)-P(2)	119.58(14)	C(10')-C(1')-C(2')	123.39(18)
C(1)-O(1)-P(2)	128.70(12)	O(1')-C(1')-C(2')	116.49(19)
C(14)-O(3)-C(15)	109.60(17)	C(3')-C(2')-C(1')	118.9(2)
C(10)-C(1)-O(1)	123.09(16)	C(2')-C(3')-C(4')	121.3(2)
C(10)-C(1)-C(2)	123.23(18)	C(3')-C(4')-C(9')	120.04(18)
O(1)-C(1)-C(2)	113.67(17)	C(3')-C(4')-C(5')	120.6(2)
C(3)-C(2)-C(1)	118.78(18)	C(9')-C(4')-C(5')	119.3(2)
C(2)-C(3)-C(4)	121.55(17)	C(6')-C(5')-C(4')	120.6(2)
C(5)-C(4)-C(3)	120.22(18)	C(5')-C(6')-C(7')	120.3(2)
C(5)-C(4)-C(9)	120.16(19)	C(8')-C(7')-C(6')	120.8(2)
C(3)-C(4)-C(9)	119.62(18)	C(7')-C(8')-C(9')	120.8(2)
C(6)-C(5)-C(4)	120.57(19)	C(8')-C(9')-C(4')	118.17(18)
C(5)-C(6)-C(7)	119.5(2)	C(8')-C(9')-C(10')	123.7(2)
C(8)-C(7)-C(6)	121.5(2)	C(4')-C(9')-C(10')	118.09(19)
C(7)-C(8)-C(9)	121.04(19)	C(1')-C(10')-C(9')	118.16(19)
C(4)-C(9)-C(8)	117.13(18)	C(1')-C(10')-C(11')	120.35(17)
C(4)-C(9)-C(10)	118.53(18)	C(9')-C(10')-C(11')	121.37(19)
C(8)-C(9)-C(10)	124.34(17)	O(2')-C(11')-N(1')	120.7(2)
C(1)-C(10)-C(9)	118.27(17)	O(2')-C(11')-C(10')	123.04(18)
C(1)-C(10)-C(11)	120.05(17)	N(1')-C(11')-C(10')	116.30(18)
C(9)-C(10)-C(11)	121.67(18)	N(1')-C(12')-C(12)	111.34(15)
O(2)-C(11)-N(1)	117.93(17)	N(2')-C(13')-C(14')	109.04(17)
O(2)-C(11)-C(10)	124.90(19)	O(3')-C(14')-C(13')	110.64(18)
N(1)-C(11)-C(10)	117.15(18)	O(3')-C(15')-C(16')	111.11(17)
N(1)-C(12)-C(12')	109.96(16)	N(2')-C(16')-C(15')	109.22(16)
N(2)-C(13)-C(14)	109.35(19)	Cl(4)-C(99)-Cl(5)	110.97(19)
O(3)-C(14)-C(13)	111.50(19)	Cl(4)-C(99)-Cl(3)	109.73(19)
O(3)-C(15)-C(16)	110.05(19)	Cl(5)-C(99)-Cl(3)	110.8(2)
N(2)-C(16)-C(15)	109.81(17)	Cl(4')-C(99')-Cl(3')	112.2(5)
C(11')-N(1')-C(12')	117.67(17)		

Table 7. Crystal data and structure refinement for **45**.

Identification code	lupo	
Empirical formula	$C_{26}\ H_{18}\ N_2\ O_8\ P_2$	
Formula weight	548.36	
Temperature	133(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 955.65(10) pm	α= 90°
	b = 1664.20(18) pm	β= 93.365(3)°
	c = 1469.92(16) pm	γ = 90°
Volume, Z	2.3337(4) nm^3, 4	
Density (calculated)	1.561 Mg/m^3	
Absorption coefficient	0.245 mm^{-1}	
F(000)	1128	
Crystal size	0.29 x 0.20 x 0.09 mm	
Theta range for data collection	1.85 to 28.53°	
Index ranges	$-12 \le h \le 12$, $-22 \le k \le 22$, $-19 \le l \le 19$	
Reflections collected	29616	
Independent reflections	5909 [$R_{Int.}$ = 0.0907]	
Completeness to theta = 28.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Data / restraints / parameters	5909 / 0 / 343	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1029	
R indices (all data)	R1 = 0.0807, wR2 = 0.1180	
Largest diff. peak and hole	537 and -406 e nm^{-3}	

Table 8. Bond lengths [Å] and angles [°] for **45**.

P'-O(1')	144.68(15)	C(5)-C(6)	138.7(3)
P'-O(4')	158.51(14)	C(6)-C(7)	137.2(3)
P'-O(3')	158.52(15)	C(9)-C(10)	135.3(3)
P'-N'	167.45(17)	C(10)-C(11)	142.2(3)
O(2')-C(1')	121.7(2)	C(11)-C(12)	142.0(3)
O(3')-C(7')	140.3(2)	C(12)-C(13)	137.3(4)
O(4')-C(9')	139.4(2)		
N'-C(1')	139.6(3)	O(1')-P'-O(4')	116.99(9)
N'-C(8')	148.3(2)	O(1')-P'-O(3')	114.45(8)
C(1')-C(2')	148.3(3)	O(4')-P'-O(3')	101.12(8)
C(2')-C(7')	138.6(3)	O(1')-P'-N'	115.42(9)
C(2')-C(3')	140.1(3)	O(4')-P'-N'	104.22(8)
C(3')-C(4')	137.7(3)	O(3')-P'-N'	102.63(8)
C(4')-C(5')	138.4(3)	C(7')-O(3')-P'	119.23(12)
C(5')-C(6')	138.0(3)	C(9')-O(4')-P'	127.75(13)
C(6')-C(7')	138.5(3)	C(1')-N'-C(8')	115.45(16)
C(8')-C(8)	152.8(3)	C(1')-N'-P'	122.00(14)
C(9')-C(10')	136.2(3)	C(8')-N'-P'	122.52(14)
C(9')-C(9)	140.9(3)	O(2')-C(1')-N'	120.49(19)
C(10')-C(11')	142.1(3)	O(2')-C(1')-C(2')	122.3(2)
C(11')-C(12')	141.4(3)	N'-C(1')-C(2')	117.17(18)
C(11')-C(11)	142.1(3)	C(7')-C(2')-C(3')	118.05(19)
C(12')-C(13')	136.9(3)	C(7')-C(2')-C(1')	122.49(19)
C(13')-C(13)	139.7(4)	C(3')-C(2')-C(1')	119.33(19)
P-O(1)	145.09(16)	C(4')-C(3')-C(2')	120.5(2)
P-O(3)	157.73(16)	C(3')-C(4')-C(5')	120.0(2)
P-O(4)	158.72(15)	C(6')-C(5')-C(4')	120.8(2)
P-N	165.84(17)	C(5')-C(6')-C(7')	118.6(2)
O(2)-C(1)	121.6(2)	C(6')-C(7')-C(2')	122.0(2)
O(3)-C(7)	140.2(2)	C(6')-C(7')-O(3')	117.52(19)
O(4)-C(9)	140.8(2)	C(2')-C(7')-O(3')	120.42(18)
N-C(1)	140.2(3)	N'-C(8')-C(8)	114.34(16)
N-C(8)	148.1(3)	C(10')-C(9')-O(4')	119.61(19)
C(1)-C(2)	147.6(3)	C(10')-C(9')-C(9)	120.60(19)
C(2)-C(7)	139.7(3)	O(4')-C(9')-C(9)	119.42(17)
C(2)-C(3)	140.1(3)	C(9')-C(10')-C(11')	120.0(2)
C(3)-C(4)	137.3(3)	C(12')-C(11')-C(10')	122.0(2)
C(4)-C(5)	139.5(3)	C(12')-C(11')-C(11)	119.0(2)

C(10')-C(11')-C(11)	118.94(19)	C(3)-C(2)-C(1)	119.46(18)
C(13')-C(12')-C(11')	120.3(2)	C(4)-C(3)-C(2)	120.8(2)
C(12')-C(13')-C(13)	120.8(2)	C(3)-C(4)-C(5)	120.2(2)
O(1)-P-O(3)	112.54(9)	C(6)-C(5)-C(4)	120.3(2)
O(1)-P-O(4)	115.41(8)	C(7)-C(6)-C(5)	118.7(2)
O(3)-P-O(4)	105.79(8)	C(6)-C(7)-C(2)	122.6(2)
O(1)-P-N	116.47(9)	C(6)-C(7)-O(3)	116.83(18)
O(3)-P-N	103.92(8)	C(2)-C(7)-O(3)	120.50(18)
O(4)-P-N	101.29(8)	N-C(8)-C(8')	114.20(17)
C(7)-O(3)-P	122.22(12)	C(10)-C(9)-O(4)	122.10(19)
C(9)-O(4)-P	120.54(12)	C(10)-C(9)-C(9')	121.32(18)
C(1)-N-C(8)	117.20(16)	O(4)-C(9)-C(9')	116.58(17)
C(1)-N-P	123.09(14)	C(9)-C(10)-C(11)	119.8(2)
C(8)-N-P	118.63(14)	C(12)-C(11)-C(11')	119.2(2)
O(2)-C(1)-N	119.82(19)	C(12)-C(11)-C(10)	121.5(2)
O(2)-C(1)-C(2)	122.93(19)	C(11')-C(11)-C(10)	119.29(19)
N-C(1)-C(2)	117.24(17)	C(13)-C(12)-C(11)	119.9(3)
C(7)-C(2)-C(3)	117.44(19)	C(12)-C(13)-C(13')	120.8(2)
C(7)-C(2)-C(1)	123.10(19)		

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x-1,-y+3/2,z+1/2 #3 -x+1,y-1/2,-z+1/2

#4 x,-y+3/2,z+1/2

Table 9. Crystal data and structure refinement for **54**.

Identification code	luna	
Empirical formula	$C_{22} H_{26} Cl_2 N_4 O_6 P_2$	
Formula weight	575.31	
Temperature	173(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 1202.85(10) pm	α= 90°.
	b = 1423.56(12) pm	β= 112.747(8)°.
	c = 1543.61(14) pm	γ = 90°.
Volume, Z	2.4376(4) nm^3 , 4	
Density (calculated)	1.568 Mg/m^3	
Absorption coefficient	0.446 mm^{-1}	
F(000)	1192	
Crystal size	0.40 x 0.40 x 0.20 mm^3	
Theta range for data collection	3.08 to 25.00°.	
Index ranges	0<=h<=14, 0<=k<=16, -18<=l<=16	
Reflections collected	4494	
Independent reflections	4283 [R(int) = 0.0263]	
Completeness to theta = 25.00°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4283 / 0 / 327	
Goodness-of-fit on F^2	0.915	
Final R indices [I>2sigma(I)]	R1 = 0.0381, wR2 = 0.0796	
R indices (all data)	R1 = 0.0664, wR2 = 0.0863	
Largest diff. peak and hole	0.429 and -0.318 $e.Å^{-3}$	

Table 10. Bond lengths [pm] and angles [°] for **54**.

P(1)-O(1)	146.09(19)	C(99)-Cl(99)	176.0(3)
P(1)-O(3)	158.93(18)		
P(1)-N(1)	164.5(2)	O(1)-P(1)-O(3)	112.88(11)
P(1)-N(2)	166.9(2)	O(1)-P(1)-N(1)	115.38(12)
O(2)-C(1)	122.3(3)	O(3)-P(1)-N(1)	106.74(11)
O(3)-C(11)	144.6(3)	O(1)-P(1)-N(2)	114.71(11)
N(1)-C(7)	141.1(3)	O(3)-P(1)-N(2)	102.96(10)
N(1)-C(8)	147.3(3)	N(1)-P(1)-N(2)	102.92(11)
N(2)-C(1)	139.0(3)	C(11)-O(3)-P(1)	122.20(16)
N(2)-C(9)	149.3(3)	C(7)-N(1)-C(8)	119.7(2)
C(1)-C(2)	148.0(4)	C(7)-N(1)-P(1)	121.28(18)
C(2)-C(7)	139.6(4)	C(8)-N(1)-P(1)	116.62(19)
C(2)-C(3)	139.8(4)	C(1)-N(2)-C(9)	118.9(2)
C(3)-C(4)	137.7(4)	C(1)-N(2)-P(1)	124.55(18)
C(4)-C(5)	137.9(4)	C(9)-N(2)-P(1)	115.77(17)
C(5)-C(6)	138.4(4)	O(2)-C(1)-N(2)	120.0(2)
C(6)-C(7)	140.3(4)	O(2)-C(1)-C(2)	123.1(2)
C(9)-C(10)	152.6(3)	N(2)-C(1)-C(2)	116.9(2)
C(10)-C(9')	152.3(3)	C(7)-C(2)-C(3)	119.5(3)
C(11)-C(11')	149.1(4)	C(7)-C(2)-C(1)	124.2(2)
P(1')-O(1')	146.08(18)	C(3)-C(2)-C(1)	116.2(2)
P(1')-O(3')	159.12(18)	C(4)-C(3)-C(2)	121.1(3)
P(1')-N(1')	165.0(2)	C(3)-C(4)-C(5)	119.5(3)
P(1')-N(2')	166.9(2)	C(4)-C(5)-C(6)	120.7(3)
O(2')-C(1')	122.2(3)	C(5)-C(6)-C(7)	120.3(3)
O(3')-C(11')	145.0(3)	C(2)-C(7)-C(6)	119.0(3)
N(1')-C(7')	141.1(3)	C(2)-C(7)-N(1)	120.8(2)
N(1')-C(8')	147.8(3)	C(6)-C(7)-N(1)	120.2(3)
N(2')-C(1')	139.0(3)	N(2)-C(9)-C(10)	112.7(2)
N(2')-C(9')	148.2(3)	C(9')-C(10)-C(9)	112.9(2)
C(1')-C(2')	147.6(3)	O(3)-C(11)-C(11')	107.2(2)
C(2')-C(7')	139.8(3)	O(1')-P(1')-O(3')	113.03(10)
C(2')-C(3')	140.4(3)	O(1')-P(1')-N(1')	114.52(11)
C(3')-C(4')	137.9(4)	O(3')-P(1')-N(1')	107.77(10)
C(4')-C(5')	138.8(4)	O(1')-P(1')-N(2')	114.94(10)
C(5')-C(6')	136.9(4)	O(3')-P(1')-N(2')	102.53(10)
C(6')-C(7')	139.7(3)	N(1')-P(1')-N(2')	102.86(10)
C(99)-Cl(98)	174.7(3)	C(11')-O(3')-P(1')	123.52(16)

C(7')-N(1')-C(8')	119.6(2)	C(3')-C(2')-C(1')	116.8(2)
C(7')-N(1')-P(1')	123.36(17)	C(4')-C(3')-C(2')	121.0(2)
C(8')-N(1')-P(1')	115.40(16)	C(3')-C(4')-C(5')	119.0(2)
C(1')-N(2')-C(9')	116.9(2)	C(6')-C(5')-C(4')	121.0(3)
C(1')-N(2')-P(1')	127.01(17)	C(5')-C(6')-C(7')	120.8(2)
C(9')-N(2')-P(1')	115.64(16)	C(6')-C(7')-C(2')	119.0(2)
O(2')-C(1')-N(2')	119.8(2)	C(6')-C(7')-N(1')	119.8(2)
O(2')-C(1')-C(2')	123.2(2)	C(2')-C(7')-N(1')	121.2(2)
N(2')-C(1')-C(2')	117.0(2)	N(2')-C(9')-C(10)	112.3(2)
C(7')-C(2')-C(3')	119.3(2)	O(3')-C(11')-C(11)	109.0(2)
C(7')-C(2')-C(1')	123.9(2)	Cl(98)-C(99)-Cl(99)	111.94(17)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+3/2,y-1/2,-z+3/2 #3 x-1/2,-y+1/2,z-1/2

#4 -x+1,-y+1,-z+1

Table 11. Crystal data and structure refinement for **54**.

Identification code	lutetia	
Empirical formula	$C_{21} H_{24} N_4 O_4 P_2 S_2$	
Formula weight	522.50	
Temperature	143(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 803.2(4) pm	α= 90°
	b = 1637.7(8) pm	β= 92.03(10)°
	c = 876.2(6) pm	γ = 90°
Volume, Z	1.1519(11) nm^3, 2	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	0.408 mm^{-1}	
F(000)	544	
Crystal size	0.25 x 0.19 x 0.15 mm	
Theta range for data collection	2.33 to 30.55°	
Index ranges	$-11 \le h \le 11$, $-23 \le k \le 23$, $-12 \le l \le 12$	
Reflections collected	14315	
Independent reflections	6983 [$R_{Int.}$ = 0.0544]	
Completeness to theta = 30.00°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Data / restraints / parameters	6983 / 1 / 300	
Goodness-of-fit on F^2	0.895	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0651	
R indices (all data)	R1 = 0.0534, wR2 = 0.0684	
Absolutstrukturparameter	-0.06(5)	
Largest diff. peak and hole	389 and -258 e nm^{-3}	

Table 12. Bond lengths [Å] and angles [°] for **54**.

P(1)-O(2)	160.07(18)	O(2)-P(1)-N(1)	106.62(9)
P(1)-N(1)	165.84(19)	O(2)-P(1)-N(2)	102.16(11)
P(1)-N(2)	167.32(18)	N(1)-P(1)-N(2)	102.94(8)
P(1)-S(1)	191.75(17)	O(2)-P(1)-S(1)	113.42(7)
O(1)-C(1)	121.7(2)	N(1)-P(1)-S(1)	115.38(7)
O(2)-C(11)	145.7(2)	N(2)-P(1)-S(1)	114.91(10)
N(1)-C(7)	140.4(3)	C(11)-O(2)-P(1)	123.46(14)
N(1)-C(8)	147.8(3)	C(7)-N(1)-C(8)	118.19(17)
N(2)-C(1)	139.6(3)	C(7)-N(1)-P(1)	123.21(14)
N(2)-C(9)	149.3(3)	C(8)-N(1)-P(1)	116.93(14)
C(1)-C(2)	148.4(3)	C(1)-N(2)-C(9)	116.63(17)
C(2)-C(3)	139.5(3)	C(1)-N(2)-P(1)	125.17(14)
C(2)-C(7)	140.4(3)	C(9)-N(2)-P(1)	117.67(14)
C(3)-C(4)	137.8(3)	O(1)-C(1)-N(2)	120.66(19)
C(4)-C(5)	137.9(3)	O(1)-C(1)-C(2)	122.07(19)
C(5)-C(6)	138.0(3)	N(2)-C(1)-C(2)	117.21(17)
C(6)-C(7)	139.5(3)	C(3)-C(2)-C(7)	119.73(19)
C(9)-C(10)	152.4(3)	C(3)-C(2)-C(1)	116.56(18)
C(10)-C(9')	152.2(3)	C(7)-C(2)-C(1)	123.54(18)
C(11)-C(11')	149.0(3)	C(4)-C(3)-C(2)	121.2(2)
P(1')-O(2')	158.41(19)	C(3)-C(4)-C(5)	118.9(2)
P(1')-N(1')	165.90(18)	C(4)-C(5)-C(6)	121.0(2)
P(1')-N(2')	167.4(2)	C(5)-C(6)-C(7)	120.93(19)
P(1')-S(1')	191.80(13)	C(6)-C(7)-C(2)	118.18(19)
O(1')-C(1')	122.3(3)	C(6)-C(7)-N(1)	120.40(18)
O(2')-C(11')	144.9(2)	C(2)-C(7)-N(1)	121.42(19)
N(1')-C(7')	140.5(2)	N(2)-C(9)-C(10)	113.62(17)
N(1')-C(8')	147.2(3)	C(9')-C(10)-C(9)	113.15(17)
N(2')-C(1')	139.0(2)	O(2)-C(11)-C(11')	108.40(17)
N(2')-C(9')	148.1(2)	O(2')-P(1')-N(1')	103.60(8)
C(1')-C(2')	147.1(3)	O(2')-P(1')-N(2')	101.60(9)
C(2')-C(3')	139.2(3)	N(1')-P(1')-N(2')	101.56(8)
C(2')-C(7')	141.3(3)	O(2')-P(1')-S(1')	114.37(8)
C(3')-C(4')	137.4(3)	N(1')-P(1')-S(1')	116.73(7)
C(4')-C(5')	137.8(3)	N(2')-P(1')-S(1')	116.83(9)
C(5')-C(6')	138.6(3)	C(11')-O(2')-P(1')	125.23(13)
C(6')-C(7')	139.3(3)	C(7')-N(1')-C(8')	118.39(17)
		C(7')-N(1')-P(1')	120.24(13)

C(8')-N(1')-P(1')	114.99(13)	C(4')-C(3')-C(2')	121.7(2)
C(1')-N(2')-C(9')	117.16(16)	C(3')-C(4')-C(5')	118.8(2)
C(1')-N(2')-P(1')	125.62(14)	C(4')-C(5')-C(6')	121.5(2)
C(9')-N(2')-P(1')	116.29(13)	C(5')-C(6')-C(7')	120.0(2)
O(1')-C(1')-N(2')	120.13(19)	C(6')-C(7')-N(1')	121.01(18)
O(1')-C(1')-C(2')	122.98(18)	C(6')-C(7')-C(2')	118.87(18)
N(2')-C(1')-C(2')	116.87(18)	N(1')-C(7')-C(2')	120.10(18)
C(3')-C(2')-C(7')	119.14(18)	N(2')-C(9')-C(10)	111.08(16)
C(3')-C(2')-C(1')	117.06(18)	O(2')-C(11')-C(11)	109.54(17)
C(7')-C(2')-C(1')	123.80(17)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x,y-1/2,-z+1

Table 13. Crystal data and structure refinement for **51**.

Identification code	lulu	
Empirical formula	$C_{30}\ H_{28}\ Cl_4\ N_4\ O_4\ P_2$	
Formula weight	712.30	
Temperature	143(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 810.72(10) pm	α= 84.432(3)°
	b = 1168.67(14) pm	β= 81.573(3)°
	c = 1750.7(2) pm	γ = 81.046(3)°
Volume, Z	1.6161(3) nm^3, 2	
Density (calculated)	1.464 Mg/m^3	
Absorption coefficient	0.508 mm^{-1}	
F(000)	732	
Crystal size	0.50 x 0.29 x 0.22 mm	
Theta range for data collection	1.18 to 30.64°	
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 16$, $-24 \le l \le 25$	
Reflections collected	36406	
Independent reflections	9899 [$R_{Int.}$ = 0.0431]	
Completeness to theta = 30.00°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2 Full-matrix)	
Data / restraints / parameters	9899 / 18 / 412	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0896	
R indices (all data)	R1 = 0.0416, wR2 = 0.0934	
Largest diff. peak and hole	848 and -593 e nm^{-3}	

Table 14. Bond lengths [Å] and angles [°] for **51**.

P-N(1)	167.76(10)	C(4')-C(5')	139.3(2)
P-O(2)	168.68(9)	C(5')-C(6')	138.89(19)
P-N(2)	170.29(10)	C(10')-C(11')	136.61(15)
O(1)-C(1)	123.27(14)	C(11')-C(12')	142.10(15)
O(2)-C(10)	138.04(12)	C(12')-C(13')	141.80(15)
N(1)-C(7)	139.86(15)	C(13')-C(14')	137.64(17)
N(1)-C(8)	147.01(15)	C(99)-Cl(2)	176.30(15)
N(2)-C(1)	137.64(14)	C(99)-Cl(1)	176.56(15)
N(2)-C(9)	147.41(14)	C(98)-Cl(3)	178.0(13)
C(1)-C(2)	147.82(16)	C(98)-Cl(4)	178.4(13)
C(2)-C(3)	140.05(16)	C(98')-Cl(4')	173.9(3)
C(2)-C(7)	140.93(16)	C(98')-Cl(3')	173.9(4)
C(3)-C(4)	138.30(19)		
C(4)-C(5)	139.0(2)	N(1)-P-O(2)	102.65(5)
C(5)-C(6)	138.44(19)	N(1)-P-N(2)	98.90(5)
C(6)-C(7)	140.51(16)	O(2)-P-N(2)	95.11(4)
C(9)-C(9')	154.08(16)	C(10)-O(2)-P	116.94(7)
C(10)-C(11)	136.63(15)	C(7)-N(1)-C(8)	119.35(10)
C(10)-C(10')	142.08(15)	C(7)-N(1)-P	123.29(8)
C(11)-C(12)	142.09(15)	C(8)-N(1)-P	115.73(8)
C(12)-C(13)	142.06(15)	C(1)-N(2)-C(9)	116.50(9)
C(12)-C(12')	142.54(15)	C(1)-N(2)-P	126.05(8)
C(13)-C(14)	137.34(17)	C(9)-N(2)-P	116.05(7)
C(14)-C(14')	141.30(18)	O(1)-C(1)-N(2)	119.85(10)
P'-N(1')	167.90(10)	O(1)-C(1)-C(2)	122.35(10)
P'-O(2')	169.17(9)	N(2)-C(1)-C(2)	117.79(10)
P'-N(2')	169.98(10)	C(3)-C(2)-C(7)	119.47(11)
O(1')-C(1')	122.96(14)	C(3)-C(2)-C(1)	117.48(10)
O(2')-C(10')	138.49(12)	C(7)-C(2)-C(1)	123.04(10)
N(1')-C(7')	139.67(15)	C(4)-C(3)-C(2)	121.33(12)
N(1')-C(8')	147.17(15)	C(3)-C(4)-C(5)	118.98(12)
C(7')-C(6')	140.44(16)	C(6)-C(5)-C(4)	121.02(12)
C(7')-C(2')	140.63(16)	C(5)-C(6)-C(7)	120.47(12)
N(2')-C(1')	137.94(14)	N(1)-C(7)-C(6)	121.05(11)
N(2')-C(9')	147.49(14)	N(1)-C(7)-C(2)	120.20(10)
C(1')-C(2')	147.73(16)	C(6)-C(7)-C(2)	118.73(11)
C(2')-C(3')	139.59(16)	N(2)-C(9)-C(9')	113.46(9)
C(3')-C(4')	138.20(19)	C(11)-C(10)-O(2)	121.05(10)

C(11)-C(10)-C(10')	120.74(10)	O(1')-C(1')-C(2')	122.35(11)
O(2)-C(10)-C(10')	118.16(9)	N(2')-C(1')-C(2')	117.52(10)
C(10)-C(11)-C(12)	120.09(10)	C(3')-C(2')-C(7')	119.71(11)
C(13)-C(12)-C(11)	121.86(10)	C(3')-C(2')-C(1')	116.83(11)
C(13)-C(12)-C(12')	119.03(10)	C(7')-C(2')-C(1')	123.44(10)
C(11)-C(12)-C(12')	119.11(10)	C(4')-C(3')-C(2')	121.63(12)
C(14)-C(13)-C(12)	120.61(11)	C(3')-C(4')-C(5')	118.67(12)
C(13)-C(14)-C(14')	120.45(11)	C(6')-C(5')-C(4')	120.89(12)
N(1')-P'-O(2')	102.42(5)	C(5')-C(6')-C(7')	120.55(12)
N(1')-P'-N(2')	99.36(5)	N(2')-C(9')-C(9)	113.03(9)
O(2')-P'-N(2')	96.93(4)	C(11')-C(10')-O(2')	121.53(9)
C(10')-O(2')-P'	114.88(7)	C(11')-C(10')-C(10)	120.58(9)
C(7')-N(1')-C(8')	119.03(10)	O(2')-C(10')-C(10)	117.88(9)
C(7')-N(1')-P'	124.72(8)	C(10')-C(11')-C(12')	120.03(10)
C(8')-N(1')-P'	114.75(8)	C(13')-C(12')-C(11')	121.68(10)
N(1')-C(7')-C(6')	121.26(11)	C(13')-C(12')-C(12)	118.92(10)
N(1')-C(7')-C(2')	120.18(10)	C(11')-C(12')-C(12)	119.39(9)
C(6')-C(7')-C(2')	118.53(11)	C(14')-C(13')-C(12')	120.80(11)
C(1')-N(2')-C(9')	115.71(9)	C(13')-C(14')-C(14)	120.16(11)
C(1')-N(2')-P'	127.78(8)	Cl(2)-C(99)-Cl(1)	111.30(8)
C(9')-N(2')-P'	116.01(7)	Cl(3)-C(98)-Cl(4)	107.1(9)
O(1')-C(1')-N(2')	120.14(11)	Cl(4')-C(98')-Cl(3')	114.6(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 x,y+1,z #3 -x,-y,-z+1

#4 -x+1,-y,-z #5 x-1,y+1,z

Table 15. Crystal data and structure refinement for **57**.

Identification code	lupino	
Empirical formula	$C_{26} H_{26} Cl_2 N_4 O_6 P_2$	
Formula weight	623.35	
Temperature	143(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 823.68(8) pm	α= 86.742(3)°
	b = 1162.18(10) pm	β= 82.843(3)°
	c = 1493.80(14) pm	γ = 71.263(3)°
Volume, Z	1.3434(2) nm^3, 2	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	0.412 mm^{-1}	
F(000)	644	
Crystal size	0.32 x 0.22 x 0.19 mm	
Theta range for data collection	1.37 to 30.03°	
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 16$, $-21 \le l \le 21$	
Reflections collected	16130	
Independent reflections	7791 [$R_{Int.}$ = 0.0345]	
Completeness to theta = 28.00°	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7791 / 7 / 381	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1298	
R indices (all data)	R1 = 0.0632, wR2 = 0.1356	
Largest diff. peak and hole	597 and -1032 e nm^{-3}	

Table 16. Bond lengths [Å] and angles [°] for **57**.

.

P(1)-O(1)	146.37(14)	C(4')-C(5')	138.4(3)
P(1)-O(3)	161.06(14)	C(5')-C(6')	138.6(3)
P(1)-N(1)	164.55(16)	C(6')-C(7')	140.0(3)
P(1)-N(2)	166.05(16)	C(11')-C(12')	138.8(3)
O(2)-C(1)	121.9(2)	C(12')-C(13')	139.0(3)
O(3)-C(11)	140.0(2)	C(99)-Cl(99)	174.8(8)
N(1)-C(7)	140.4(2)	C(99)-Cl(98)	174.6(6)
N(1)-C(8)	147.3(2)	C(99')-Cl(97)	168.3(10)
N(2)-C(1)	140.0(2)	C(99')-Cl(96)	174.7(13)
N(2)-C(9)	148.7(2)		
C(1)-C(2)	148.0(3)	O(1)-P(1)-O(3)	111.00(8)
C(2)-C(3)	140.0(3)	O(1)-P(1)-N(1)	115.21(8)
C(2)-C(7)	140.7(3)	O(3)-P(1)-N(1)	106.68(8)
C(3)-C(4)	138.0(3)	O(1)-P(1)-N(2)	115.72(8)
C(4)-C(5)	139.1(3)	O(3)-P(1)-N(2)	103.28(8)
C(5)-C(6)	139.3(3)	N(1)-P(1)-N(2)	103.86(8)
C(6)-C(7)	140.1(3)	C(11)-O(3)-P(1)	121.65(12)
C(9)-C(10)	152.3(3)	C(7)-N(1)-C(8)	119.52(15)
C(10)-C(9')	153.3(3)	C(7)-N(1)-P(1)	125.30(13)
C(11)-C(12)	138.6(3)	C(8)-N(1)-P(1)	115.09(13)
C(11)-C(11')	138.8(3)	C(1)-N(2)-C(9)	116.36(15)
C(12)-C(13)	139.0(3)	C(1)-N(2)-P(1)	127.64(13)
C(13)-C(13')	139.3(3)	C(9)-N(2)-P(1)	115.99(12)
P(1')-O(1')	145.97(15)	O(2)-C(1)-N(2)	119.47(17)
P(1')-O(3')	160.70(15)	O(2)-C(1)-C(2)	123.20(17)
P(1')-N(1')	164.09(17)	N(2)-C(1)-C(2)	117.33(16)
P(1')-N(2')	166.83(17)	C(3)-C(2)-C(7)	119.85(17)
O(2')-C(1')	122.7(2)	C(3)-C(2)-C(1)	116.45(17)
O(3')-C(11')	139.4(2)	C(7)-C(2)-C(1)	123.68(16)
N(1')-C(7')	140.9(2)	C(4)-C(3)-C(2)	121.27(19)
N(1')-C(8')	146.9(3)	C(3)-C(4)-C(5)	118.80(18)
N(2')-C(1')	139.0(2)	C(4)-C(5)-C(6)	121.19(18)
N(2')-C(9')	148.5(2)	C(5)-C(6)-C(7)	120.10(18)
C(1')-C(2')	148.7(3)	C(6)-C(7)-N(1)	120.07(17)
C(2')-C(7')	140.6(3)	C(6)-C(7)-C(2)	118.78(17)
C(2')-C(3')	141.0(3)	N(1)-C(7)-C(2)	121.06(16)
C(3')-C(4')	138.0(3)	N(2)-C(9)-C(10)	111.18(15)

C(9)-C(10)-C(9')	113.58(16)	O(2')-C(1')-C(2')	121.84(18)
C(12)-C(11)-C(11')	120.15(17)	N(2')-C(1')-C(2')	117.10(16)
C(12)-C(11)-O(3)	120.61(17)	C(7')-C(2')-C(3')	118.88(18)
C(11')-C(11)-O(3)	119.20(16)	C(7')-C(2')-C(1')	123.91(17)
C(11)-C(12)-C(13)	119.56(18)	C(3')-C(2')-C(1')	117.04(18)
C(12)-C(13)-C(13')	120.27(18)	C(4')-C(3')-C(2')	121.0(2)
O(1')-P(1')-O(3')	114.79(8)	C(3')-C(4')-C(5')	119.6(2)
O(1')-P(1')-N(1')	115.13(9)	C(4')-C(5')-C(6')	120.9(2)
O(3')-P(1')-N(1')	107.47(8)	C(5')-C(6')-C(7')	120.1(2)
O(1')-P(1')-N(2')	116.45(9)	C(6')-C(7')-C(2')	119.51(18)
O(3')-P(1')-N(2')	97.67(8)	C(6')-C(7')-N(1')	120.42(18)
N(1')-P(1')-N(2')	103.35(8)	C(2')-C(7')-N(1')	120.07(17)
C(11')-O(3')-P(1')	123.70(12)	N(2')-C(9')-C(10)	112.56(15)
C(7')-N(1')-C(8')	120.37(16)	C(12')-C(11')-C(11)	120.54(17)
C(7')-N(1')-P(1')	117.91(13)	C(12')-C(11')-O(3')	121.79(17)
C(8')-N(1')-P(1')	121.35(14)	C(11)-C(11')-O(3')	117.41(16)
C(1')-N(2')-C(9')	120.02(16)	C(11')-C(12')-C(13')	119.38(19)
C(1')-N(2')-P(1')	120.72(13)	C(12')-C(13')-C(13)	120.06(18)
C(9')-N(2')-P(1')	118.15(13)	Cl(99)-C(99)-Cl(98)	110.2(4)
O(2')-C(1')-N(2')	121.02(18)	Cl(97)-C(99')-Cl(96)	116.6(8)

Symmetry transformations used to generate equivalent atoms:

#1 x,y-1,z #2 -x+1,-y+1,-z #3 x+1,y,z #4 -x+1,-y+1,-z+1

#5 -x+2,-y+1,-z

Table 17. Crystal data and structure refinement for **58**.

Identification code	lumpi	
Empirical formula	$C_{29}\ H_{26}\ Cl_2\ N_4\ O_6\ P_2$	
Formula weight	659.38	
Temperature	173(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 1707.35(12) pm	α= 90°
	b = 1707.20(12) pm	β= 102.648(3)°
	c = 1004.54(8) pm	γ = 90°
Volume, Z	2.8570(4) nm^3, 4	
Density (calculated)	1.533 Mg/m^3	
Absorption coefficient	0.392 mm^{-1}	
F(000)	1360	
Crystal size	0.34 x 0.23 x 0.15 mm	
Theta range for data collection	1.71 to 30.55°	
Index ranges	$-24 \le h \le 24$, $-24 \le k \le 24$, $-14 \le l \le 14$	
Reflections collected	28140	
Independent reflections	4381 [$R_{Int.}$ = 0.0542]	
Completeness to theta = 30.00°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Daten / Restraints / Parameter	4381 / 0 / 196	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1166	
R indices (all data)	R1 = 0.0588, wR2 = 0.1243	
Largest diff. peak and hole	814 and -632 e nm^{-3}	

Table 18. Bond lengths [Å] and angles [°] for **57**.

P-O(1)	146.43(11)	N(1)-P-N(2)	103.64(6)
P-O(3)	160.57(11)	C(7)-N(1)-C(8)	118.88(12)
P-N(1)	164.21(13)	C(7)-N(1)-P	124.12(10)
P-N(2)	166.23(13)	C(8)-N(1)-P	116.54(10)
N(1)-C(7)	140.43(18)	C(1)-N(2)-C(9)	117.01(12)
N(1)-C(8)	147.60(19)	C(1)-N(2)-P	127.85(10)
N(2)-C(1)	138.90(18)	C(9)-N(2)-P	114.88(9)
N(2)-C(9)	147.97(17)	C(10)-O(3)-P	120.10(9)
O(2)-C(1)	121.99(18)	O(2)-C(1)-N(2)	119.92(13)
O(3)-C(10)	140.01(17)	O(2)-C(1)-C(2)	122.94(13)
C(1)-C(2)	147.91(19)	N(2)-C(1)-C(2)	117.13(13)
C(2)-C(3)	140.0(2)	C(3)-C(2)-C(7)	119.65(13)
C(2)-C(7)	140.5(2)	C(3)-C(2)-C(1)	116.87(13)
C(3)-C(4)	138.3(2)	C(7)-C(2)-C(1)	123.48(13)
C(4)-C(5)	138.8(2)	C(4)-C(3)-C(2)	121.01(15)
C(5)-C(6)	137.9(2)	C(3)-C(4)-C(5)	119.10(14)
C(6)-C(7)	140.32(19)	C(6)-C(5)-C(4)	120.98(14)
C(9)-C(9)#1	153.7(3)	C(5)-C(6)-C(7)	120.56(15)
C(10)-C(11)	136.3(2)	C(6)-C(7)-N(1)	119.84(13)
C(10)-C(10)#1	141.7(3)	C(6)-C(7)-C(2)	118.67(13)
C(11)-C(12)	141.6(2)	N(1)-C(7)-C(2)	121.42(12)
C(12)-C(13)	141.5(2)	N(2)-C(9)-C(9)#1	111.62(14)
C(12)-C(12)#1	142.9(3)	C(11)-C(10)-O(3)	120.88(12)
C(13)-C(14)	136.3(2)	C(11)-C(10)-C(10)#1	120.91(8)
C(14)-C(14)#1	141.6(3)	O(3)-C(10)-C(10)#1	118.17(7)
Cl-C(99)	178.09(19)	C(10)-C(11)-C(12)	119.74(13)
C(99)-Cl#2	178.09(19)	C(13)-C(12)-C(11)	122.05(13)
		C(13)-C(12)-C(12)#1	118.61(9)
O(1)-P-O(3)	111.46(6)	C(11)-C(12)-C(12)#1	119.34(8)
O(1)-P-N(1)	114.62(7)	C(14)-C(13)-C(12)	121.26(14)
O(3)-P-N(1)	108.55(6)	C(13)-C(14)-C(14)#1	120.13(9)
O(1)-P-N(2)	116.64(7)	Cl#2-C(99)-Cl	111.29(16)
O(3)-P-N(2)	100.70(6)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 -x+1,y,-z+1/2

Table 19. Crystal data and structure refinement for **59**.

Identification code	lunte	
Empirical formula	$C_{29}\ H_{26}\ N_4\ O_6\ P_2$	
Formula weight	588.48	
Temperature	143(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 838.86(14) pm	α= 109.845(6)°
	b = 1120.79(18) pm	β= 90.322(6)°
	c = 1487.2(2) pm	γ = 98.763(6)°
Volume, Z	1.2973(4) nm^3, 2	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	0.222 mm^{-1}	
F(000)	612	
Crystal size	0.18 x 0.17 x 0.04 mm	
Theta range for data collection	1.46 to 28.28°	
Index ranges	$-11 \le h \le 11, -14 \le k \le 14, -19 \le l \le 19$	
Reflections collected	18916	
Independent reflections	6407 [$R_{Int.}$= 0.0787]	
Completeness to theta = 28.00°	99.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Data / restraints / parameters	6407 / 0 / 372	
Goodness-of-fit on F^2	0.910	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.0876	
R indices (all data)	R1 = 0.1021, wR2 = 0.1028	
Largest diff. peak and hole	716 and -435 e nm^{-3}	

Table 20. Bond lengths [Å] and angles [°] for **59**.

P-O(1)	145.64(17)	C(2')-C(7')	141.0(3)
P-O(3)	161.94(16)	C(3')-C(4')	138.1(3)
P-N(1)	163.74(19)	C(4')-C(5')	137.8(3)
P-N(2)	166.1(2)	C(5')-C(6')	137.6(3)
O(2)-C(1)	121.4(3)	C(6')-C(7')	139.3(3)
O(3)-C(11)	140.5(3)	C(11')-C(12')	136.5(3)
N(1)-C(7)	141.0(3)	C(12')-C(13')	141.6(3)
N(1)-C(8)	147.4(3)	C(13')-C(14')	142.0(3)
N(2)-C(1)	139.9(3)	C(14')-C(15')	138.1(4)
N(2)-C(9)	148.7(3)		
C(1)-C(2)	147.6(3)	O(1)-P-O(3)	109.42(9)
C(2)-C(3)	139.5(3)	O(1)-P-N(1)	115.97(10)
C(2)-C(7)	140.1(3)	O(3)-P-N(1)	106.08(9)
C(3)-C(4)	137.8(3)	O(1)-P-N(2)	116.35(9)
C(4)-C(5)	138.1(3)	O(3)-P-N(2)	103.81(9)
C(5)-C(6)	138.8(3)	N(1)-P-N(2)	104.08(9)
C(6)-C(7)	139.5(3)	C(11)-O(3)-P	118.98(14)
C(9)-C(10)	151.4(3)	C(7)-N(1)-C(8)	118.71(18)
C(10)-C(9')	152.6(3)	C(7)-N(1)-P	125.60(16)
C(11)-C(12)	135.8(3)	C(8)-N(1)-P	115.69(15)
C(11)-C(11')	140.4(3)	C(1)-N(2)-C(9)	115.96(18)
C(12)-C(13)	141.2(3)	C(1)-N(2)-P	127.43(16)
C(13)-C(13')	141.2(3)	C(9)-N(2)-P	116.32(14)
C(13)-C(14)	142.1(3)	O(2)-C(1)-N(2)	119.7(2)
C(14)-C(15)	137.0(4)	O(2)-C(1)-C(2)	122.9(2)
C(15)-C(15')	137.5(4)	N(2)-C(1)-C(2)	117.4(2)
P'-O(1')	145.34(17)	C(3)-C(2)-C(7)	119.7(2)
P'-O(3')	160.64(18)	C(3)-C(2)-C(1)	116.6(2)
P'-N(1')	163.55(19)	C(7)-C(2)-C(1)	123.7(2)
P'-N(2')	166.05(17)	C(4)-C(3)-C(2)	121.1(2)
O(2')-C(1')	121.9(2)	C(3)-C(4)-C(5)	119.0(2)
O(3')-C(11')	138.8(3)	C(4)-C(5)-C(6)	121.1(2)
N(1')-C(7')	140.5(3)	C(5)-C(6)-C(7)	120.1(2)
N(1')-C(8')	146.9(3)	C(6)-C(7)-C(2)	118.9(2)
N(2')-C(1')	139.2(3)	C(6)-C(7)-N(1)	120.0(2)
N(2')-C(9')	148.4(3)	C(2)-C(7)-N(1)	121.1(2)
C(1')-C(2')	148.6(3)	N(2)-C(9)-C(10)	111.67(18)
C(2')-C(3')	138.6(3)	C(9)-C(10)-C(9')	113.60(19)

C(12)-C(11)-C(11')	120.3(2)	O(2')-C(1')-C(2')	121.4(2)
C(12)-C(11)-O(3)	121.4(2)	N(2')-C(1')-C(2')	117.36(18)
C(11')-C(11)-O(3)	118.3(2)	C(3')-C(2')-C(7')	118.7(2)
C(11)-C(12)-C(13)	120.0(2)	C(3')-C(2')-C(1')	117.16(19)
C(12)-C(13)-C(13')	120.0(2)	C(7')-C(2')-C(1')	123.9(2)
C(12)-C(13)-C(14)	121.3(2)	C(4')-C(3')-C(2')	121.8(2)
C(13')-C(13)-C(14)	118.7(2)	C(5')-C(4')-C(3')	118.9(2)
C(15)-C(14)-C(13)	120.4(2)	C(6')-C(5')-C(4')	121.0(2)
C(14)-C(15)-C(15')	120.8(2)	C(5')-C(6')-C(7')	120.4(2)
O(1')-P'-O(3')	114.68(9)	C(6')-C(7')-N(1')	120.97(19)
O(1')-P'-N(1')	114.56(10)	C(6')-C(7')-C(2')	119.2(2)
O(3')-P'-N(1')	106.92(10)	N(1')-C(7')-C(2')	119.9(2)
O(1')-P'-N(2')	117.43(10)	N(2')-C(9')-C(10)	113.12(19)
O(3')-P'-N(2')	97.10(9)	C(12')-C(11')-O(3')	121.6(2)
N(1')-P'-N(2')	104.18(9)	C(12')-C(11')-C(11)	121.1(2)
C(11')-O(3')-P'	124.87(14)	O(3')-C(11')-C(11)	116.92(19)
C(7')-N(1')-C(8')	120.50(18)	C(11')-C(12')-C(13')	119.9(2)
C(7')-N(1')-P'	117.79(15)	C(13)-C(13')-C(12')	118.6(2)
C(8')-N(1')-P'	121.34(15)	C(13)-C(13')-C(14')	119.4(2)
C(1')-N(2')-C(9')	120.01(17)	C(12')-C(13')-C(14')	122.0(2)
C(1')-N(2')-P'	119.36(15)	C(15')-C(14')-C(13')	119.5(3)
C(9')-N(2')-P'	118.96(14)	C(15)-C(15')-C(14')	121.1(2)
O(2')-C(1')-N(2')	121.2(2)		

Table 21. Crystal data and structure refinement for **61**.

Identification code	luxor	
Empirical formula	$C_{30}\ H_{24}\ D_2\ Cl_6\ N_4\ O_4\ P_2\ S_2$	
Formula weight	846.32	
Temperature	143(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 1837.57(14) pm	α= 90°
	b = 1851.39(14) pm	β= 92.953(3)°
	c = 1012.64(8) pm	γ = 90°
Volume, Z	3.4405(5) nm^3, 4	
Density (calculated)	1.634 Mg/m^3	
Absorption coefficient	0.758 mm^{-1}	
F(000)	1720	
Crystal size	0.38 x 0.05 x 0.05 mm	
Theta range for data collection	1.56 to 26.38°	
Index ranges	$-22 \le h \le 22, -22 \le k \le 23, -12 \le l \le 12$	
Reflections collected	38932	
Independent reflections	7049 [$R_{Int.}$ = 0.0771]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2 (Full-matrix)	
Data / restraints / parameters	7049 / 0 / 435	
Goodness-of-fit on F^2	0.948	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0699	
R indices (all data)	R1 = 0.0694, wR2 = 0.0796	
Largest diff. peak and hole	487 and -446 e nm^{-3}	

Table 22. Bond lengths [Å] and angles [°] for **61**.

P'-O(2')	160.90(16)	C(3)-C(4)	137.4(4)
P'-N(1')	165.2(2)	C(4)-C(5)	138.3(4)
P'-N(2')	167.7(2)	C(5)-C(6)	138.0(4)
P'-S'	192.40(9)	C(6)-C(7)	138.9(4)
O(1')-C(1')	122.8(3)	C(10)-C(11)	135.6(3)
O(2')-C(10')	141.0(3)	C(11)-C(12)	142.0(3)
N(1')-C(7')	140.9(3)	C(12)-C(13)	142.2(3)
N(1')-C(8')	147.7(3)	C(13)-C(14)	135.9(3)
N(2')-C(1')	139.5(3)	C(99)-Cl(3)	175.6(3)
N(2')-C(9')	148.6(3)	C(99)-Cl(2)	175.7(3)
C(1')-C(2')	146.2(4)	C(99)-Cl(1)	176.9(3)
C(2')-C(3')	140.5(3)	C(98)-Cl(6)	175.8(3)
C(2')-C(7')	140.6(3)	C(98)-Cl(5)	175.9(3)
C(3')-C(4')	137.4(4)	C(98)-Cl(4)	176.4(3)
C(4')-C(5')	138.6(4)		
C(5')-C(6')	138.0(3)	O(2')-P'-N(1')	105.03(10)
C(6')-C(7')	139.2(4)	O(2')-P'-N(2')	101.55(9)
C(9')-C(9)	153.2(3)	N(1')-P'-N(2')	102.34(10)
C(10')-C(11')	136.6(3)	O(2')-P'-S'	112.45(7)
C(10')-C(10)	141.4(3)	N(1')-P'-S'	117.05(8)
C(11')-C(12')	141.5(3)	N(2')-P'-S'	116.57(8)
C(12')-C(13')	141.8(3)	C(10')-O(2')-P'	124.44(14)
C(12')-C(12)	142.0(4)	C(7')-N(1')-C(8')	118.4(2)
C(13')-C(14')	137.0(3)	C(7')-N(1')-P'	125.74(17)
C(14')-C(14)	140.5(4)	C(8')-N(1')-P'	115.43(16)
P-O(2)	161.94(16)	C(1')-N(2')-C(9')	115.9(2)
P-N(1)	164.4(2)	C(1')-N(2')-P'	127.49(18)
P-N(2)	166.8(2)	C(9')-N(2')-P'	116.26(16)
P-S	192.17(9)	O(1')-C(1')-N(2')	119.1(2)
O(1)-C(1)	121.8(3)	O(1')-C(1')-C(2')	123.1(2)
O(2)-C(10)	140.2(3)	N(2')-C(1')-C(2')	117.8(2)
N(1)-C(7)	141.2(3)	C(3')-C(2')-C(7')	119.0(2)
N(1)-C(8)	148.4(3)	C(3')-C(2')-C(1')	117.0(2)
N(2)-C(1)	139.2(3)	C(7')-C(2')-C(1')	123.9(2)
N(2)-C(9)	148.9(3)	C(4')-C(3')-C(2')	121.5(2)
C(1)-C(2)	147.6(4)	C(3')-C(4')-C(5')	118.7(2)
C(2)-C(3)	139.7(3)	C(6')-C(5')-C(4')	121.4(3)
C(2)-C(7)	141.1(3)	C(5')-C(6')-C(7')	120.3(2)

C(6')-C(7')-C(2')	119.0(2)	C(11')-C(12')-C(13')	121.7(2)
C(6')-C(7')-N(1')	120.3(2)	C(11')-C(12')-C(12)	119.0(2)
C(2')-C(7')-N(1')	120.6(2)	C(13')-C(12')-C(12)	119.2(2)
N(2')-C(9')-C(9)	112.1(2)	C(14')-C(13')-C(12')	120.3(3)
C(11')-C(10')-O(2')	120.9(2)	C(13')-C(14')-C(14)	120.3(2)
C(11')-C(10')-C(10)	120.2(2)	O(2)-P-N(1)	108.98(10)
O(2')-C(10')-C(10)	118.9(2)	O(2)-P-N(2)	98.06(9)
C(10')-C(11')-C(12')	120.4(2)	N(1)-P-N(2)	102.91(10)
O(2)-P-S	112.99(7)	N(2)-C(1)-C(2)	117.4(2)
N(1)-P-S	115.09(8)	C(3)-C(2)-C(7)	119.0(2)
N(2)-P-S	117.07(8)	C(3)-C(2)-C(1)	117.2(2)
C(10)-O(2)-P	123.69(14)	C(7)-C(2)-C(1)	123.8(2)
C(7)-N(1)-C(8)	117.0(2)	C(4)-C(3)-C(2)	121.5(3)
C(7)-N(1)-P	124.05(16)	C(3)-C(4)-C(5)	119.0(3)
C(8)-N(1)-P	118.78(17)	C(6)-C(5)-C(4)	120.9(3)
C(1)-N(2)-C(9)	116.28(19)	C(5)-C(6)-C(7)	120.7(2)
C(1)-N(2)-P	127.07(17)	C(6)-C(7)-C(2)	118.8(2)
C(9)-N(2)-P	115.60(16)	C(6)-C(7)-N(1)	120.9(2)
O(1)-C(1)-N(2)	119.9(2)	C(2)-C(7)-N(1)	120.2(2)
O(1)-C(1)-C(2)	122.6(2)		
N(2)-C(9)-C(9')	110.9(2)	C(12')-C(12)-C(11)	119.2(2)
C(11)-C(10)-O(2)	120.3(2)	C(12')-C(12)-C(13)	118.7(2)
C(11)-C(10)-C(10')	121.0(2)	C(11)-C(12)-C(13)	122.2(2)
O(2)-C(10)-C(10')	118.5(2)	C(14)-C(13)-C(12)	120.6(3)
C(10)-C(11)-C(12)	120.1(2)	C(13)-C(14)-C(14')	120.9(2)
Cl(3)-C(99)-Cl(2)	110.71(15)		
Cl(3)-C(99)-Cl(1)	109.66(15)		
Cl(2)-C(99)-Cl(1)	110.64(16)		
Cl(6)-C(98)-Cl(5)	110.20(15)		
Cl(6)-C(98)-Cl(4)	109.71(14)		
Cl(5)-C(98)-Cl(4)	110.30(15		

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z+1 #2 -x,-y+1,-z+2 #3 x,-y+1/2,z-1/2

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13. Curriculum Vitae

Personalien:

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Aug. 1990 - Feb. 1993	wissenschaftliche Mitarbeiterin beim Shanghai Institute of Daily Chemicals and Industry.
März 1993 - April 1996	Area Representitive bei BASF Shanghai. Koordination zwischen BASF und chinesischen Partnern Entwicklung von Marketingstrategie. Durchführen von Trainings und Seminaren bei Kunden.
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1974 - 1979	Grundschule, Shanghai.
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Sep. 1985 - Jul. 1990	Chemiestudium an der Tongji-Universität, Shanghai. Schwerpunkt: Technische Chemie.
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Sonstiges:

Sept.1994 - Okt. 1994	Training für technische Consulting im Bereich Vertrieb und Marketing bei BASF Ludwighafen.
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Sprache:

Chinesisch
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